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ELEMENTS  
OF  
C H E M I S T R Y.

FOR THE  
USE OF COLLEGES, ACADEMIES, AND SCHOOLS.

By M. V. REGNAULT.

ILLUSTRATED BY NEARLY SEVEN HUNDRED WOOD-CUTS.

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TRANSLATED FROM THE FRENCH,  
By T. FORREST BETTON, M.D., M.A.N.S.

FELLOW OF THE COLLEGE OF PHYSICIANS OF PHILADELPHIA, ETC.

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AND EDITED WITH NOTES,  
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SECOND EDITION.

TO WHICH IS APPENDED A COMPARATIVE TABLE OF FRENCH AND ENGLISH  
WEIGHTS AND MEASURES.

IN TWO VOLUMES.—VOL. II.

PHILADELPHIA:  
CLARK & HESSER.  
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## TABLE OF CONTENTS OF VOL. II.

	PAGE		PAGE
PREPARATION OF ORES.....	9	IRON, composition of bar and cast-iron,	
Washing.....	10	and steel.....	116
Crushing by cylinders.....	11	CHROMIUM, oxides of.....	118
Swing-sieve.....	15	" chromic acid.....	122
Jigging-machine.....	16	" salts of.....	123
Stamping ore.....	17	" chromates.....	125
Deposit-trough.....	18	" analytic determination of..	128
Sleeping-table, or nicking-buddle.....	19	COBALT, metal and oxides.....	130
Percussion-table, or brake-table.....	20	" salts of.....	131
MANGANESE.....	23	" arsenical ores.....	132
" oxides of.....	23	" analytic determination of.....	133
" acids of.....	25	" <i>smalt and saffre</i> .....	134
" salts of.....	28	" Thenard's blue.....	135
" sulphide and chloride of.....	29	NICKEL, metal and oxides of.....	136
" analytic determination of.....	31	" salts of.....	137
IRON, metallic.....	36	" German silver.....	138
" oxides of.....	40	" analytic determination of.....	139
" salts of.....	44	ZINC, distillation of.....	141
" sulphide of.....	47	" oxide of.....	142
" chloride of.....	49	" salts of.....	143
" cyanides of.....	50	" sulphide and chloride of.....	144
" carburet of, cast-iron.....	53	" analytic determination of.....	144
" analytic determination of.....	54	" <i>metallurgy of</i> .....	146
" ores of.....	59	" " in Belgium.....	147
" reduction of its ores, by the Cata-		" " in Silesia.....	150
lonian forge.....	61	" " in England.....	151
<i>Reduction in the blast-furnace</i> .....	66	CADMIUM, compounds of.....	153
" the blast.....	67	" analytic determination of.....	154
" mixing ores.....	70	TIN.....	156
" blowing the furnace.....	71	" oxides of.....	158
" hot-blast.....	77	" salts of.....	160
" waste-heat of blast-furnace.....	78	" sulphides of.....	161
" remelting pig-metal.....	80	" chlorides of.....	162
" conversion of cast into bar-iron....	82	" behaviour of salts of.....	164
" refining on the forge-hearth.....	83	" <i>metallurgy of</i> .....	166
" " by puddling.....	87	TITANIUM.....	169
" blooming and rolling.....	92	" oxides of.....	170
" Making sheet and tin plate.....	99	" chlorides of.....	171
" wire-drawing.....	101	COLUMBIUM, NIOBIUM, PELOPIUM, IL-	
" making steel.....	102	MENIUM.....	174
" " forge steel.....	103	LEAD.....	174
" " blistered and cast-steel..	104	" oxides of, litharge.....	175
" tempering steel.....	107	" red, or minium.....	178
" dry assay of iron-ores.....	108	" salts of.....	179
" analysis of cast, and steel.....	111	" acetates of, sugar of lead.....	183

	PAGE		PAGE
LEAD, carbonate of, white-lead.....	184	MERCURY, chlorides of, calomel.....	282
“ behaviour of salts of.....	186	“ “ corrosive subli- mate.....	284
“ sulphide of.....	186	“ “ white precipitate.....	285
“ chloride of.....	188	“ iodides of.....	286
“ analytic determination of.....	188	“ cyanide of.....	287
“ alloys, type-metal, and soft solder.....	189	“ analytic determination of.....	288
“ metallurgy of.....	190	“ amalgams of, mirrors.....	289
“ “ reduction by iron.....	192	“ metallurgy of, in Idria.....	290
“ “ reverberatory pro- cess.....	196	“ “ at Almaden.....	291
“ “ Scotch hearth.....	198	SILVER.....	293
“ “ cupellation.....	198	“ oxides of.....	294
“ “ Pattinson's process..	202	“ fulminating.....	295
“ making sheet, and pipe.....	202	“ salts of.....	296
“ casting shot.....	203	“ “ lunar caustic.....	297
BISMUTH.....	204	“ sulphides of.....	300
“ oxides of.....	205	“ chlorides of.....	301
“ salts of, pearl-white.....	206	“ analytic determination of.....	303
“ alloys of, fusible metal.....	208	“ metallurgy of.....	304
“ analytic determination of.....	208	“ “ Freiberg process...	305
“ metallurgy of.....	209	“ “ Mansfeld “	309
ANTIMONY.....	211	“ “ American “	310
“ oxides and acids of.....	212	“ alloys of.....	311
“ salts of.....	214	“ “ coin and plate.....	312
“ sulphides of, Kermes mineral	215	“ assay of alloys of, by cupella- tion.....	313
“ chlorides of.....	217	“ assay of alloys of, in the wet way.....	316
“ behaviour of salts of.....	218	“ assay of ores of.....	321
“ analytic determination of.....	219	GOLD and its compounds.....	322
“ detection of, in poisoning.....	221	“ purple of Cassius.....	325
“ alloys of.....	221	“ analytic determination of.....	326
“ metallurgy of.....	222	“ metallurgy of.....	326
URANIUM, and its oxides.....	224	“ “ Tyrolese bowls.....	328
“ salts of.....	225	“ alloys of.....	329
“ analytic determination of.....	228	“ separation of, and silver, by sul- phuric acid.....	329
TUNGSTEN, and its oxides.....	230	“ separation of, and silver, by ni- tric acid.....	331
“ analytic determination of.....	232	“ gilding and silvering.....	331
MOLYBDENUM, its oxides and salts.....	233	“ “ “ by immer- sion.....	332
VANADIUM.....	235	“ galvanic gilding.....	333
COPPER.....	236	“ “ silvering.....	334
“ oxides of.....	237	“ galvanoplastics.....	335
“ salts of.....	239	“ assay of alloys of, by quartation.	336
“ “ blue vitriol.....	240	“ “ “ by the touch- needle.....	338
“ “ mineral and Scheele's green.....	242	PLATINUM.....	339
“ “ verdigris.....	243	“ black.....	340
“ sulphides of.....	243	“ flameless lamp.....	341
“ chlorides of.....	244	“ oxides of.....	342
“ analytic determination of.....	245	“ salts of.....	343
“ metallurgy of.....	247	“ chlorides of.....	345
“ “ Mansfeld process..	249	“ ammonia-bases of.....	346
“ “ eliquation of silver	251	“ analytic determination of.....	347
“ “ English process....	256	“ extraction of.....	349
“ alloys of, and zinc.....	263	OSMIUM.....	350
“ “ “ brass.....	264	“ compounds of.....	351
“ “ tin, bronze.....	265	“ extraction of.....	352
“ “ cannon-casting	266	IRIDIUM.....	353
“ “ tinning copper and brass.....	269	“ compounds of.....	354
“ analysis of brass and bronze.....	270	PALLADIUM, and its compounds.....	356
MERCURY.....	271	RHODIUM, and its compounds.....	358
“ purification of.....	272	RUTHENIUM.....	360
“ oxides of.....	273		
“ salts of.....	275		
“ fulminating.....	279		
“ amide-base of.....	279		
“ sulphides of, cinnabar.....	281		

## FOURTH PART.

## ORGANIC CHEMISTRY.

	PAGE		PAGE
INTRODUCTION.....	361-445	ESSENTIAL PROXIMATE PRINCIPLES OF	
Organized and organic bodies.....	362	PLANTS.....	446
Proximate analysis of organic sub-		<i>Cellulose</i> .....	446
stances.....	363	Lignin.....	449
<i>Ultimate analysis of organic sub-</i>		<i>Albuminous Vegetable Substances</i> .....	451
<i>stances</i> .....	366	Albumen.....	453
Ultimate analysis, determination of		Circular polarization (note).....	454
carbon and hydrogen.....	367	Gluten, vegetable fibrin, and casein...	460
Ultimate analysis, desiccation.....	369	<i>Amylaceous Substances</i> .....	461
“ “ combustion.....	371	Inulin and lichenin.....	467
“ “ of non-volatile li-		Gums, arabin, cerasin, bassorin.....	468
quids.....	374	<i>Sugar</i> .....	469
“ “ of volatile sub-		Cane-sugar.....	470
stances.....	375	Caramel, saccharic acid.....	471
“ “ of gaseous organic		Fruit-sugar.....	474
bodies.....	375	Grape-sugar.....	475
“ “ determination of		Glucic acid.....	476
carbonic acid by		Determination of sugar by oxide of cop-	
volume.....	377	per.....	477
“ “ determination of		Determination of sugar by polarization	478
nitrogen by vo-		<i>Gelatinous Principles</i> , pectose.....	478
lume.....	380	Pectin and pectic acid.....	479
Ultimate analysis, determination of		Table of pectic acids.....	483
nitrogen as ammonia.....	382	Mannite.....	484
Ultimate analysis, determination of		<i>Action of Acids on Lignin, Starch, and</i>	
sulphur.....	385	<i>Sugar</i> .....	485
Ultimate analysis, determination of		Dextrin.....	485
phosphorus.....	385	British gum.....	486
Ultimate analysis, determination of		Diastase.....	487
chlorine, bromine, iodine, and oxy-		Glucose, manufacture of.....	487
gen.....	386	Ulmin and humin.....	489
<i>Construction of a formula for an organic</i>		<i>Action of nitric acid, oxysaccharic</i>	
substance.....	387	acid.....	491
“ “ when it is acid	387	Gun-cotton.....	491
“ “ from its mine-		Collodion.....	492
ral base.....	393	Mucic acid.....	493
“ “ when it is basic	397	<i>Spontaneous Decomposition of Plants</i> ...	494
“ “ when neither		Mineral fuel.....	494
acid nor basic	399	Varieties of coal.....	496
Determination of density of vapours.....	406	Analysis “.....	497
Simultaneous temperatures in thermo-		Tables of composition of coal....	500, 503
meters differently constructed.....	413	<i>Alcoholic Fermentation</i> .....	505
Air-thermometer (note).....	414	Yeast or ferment.....	507
<i>Analysis of gases</i> , apparatus for.....	422	Alcohol.....	511
“ “ absorbing reagents...	430	Alcoholometry.....	513
“ “ examples of.....	433	Sulphovinic acid.....	515
“ “ oxygen and nitrogen	433	Ether.....	516
Analysis of gases, oxygen, nitrogen,		Olefiant gas.....	520
and hydrogen.....	435	Ethionic acid.....	522
Analysis of gases, oxygen, nitrogen, and		Dutch liquid.....	523
carbonic oxide.....	436	Chlorinated olefiant gas.....	524
Analysis of gases, oxygen, carburetted		Oil of wine.....	528
hydrogen, etc.....	437	Ethers and vinic acids.....	529
Analysis of gases, complex mixtures....	443	Phosphovinic acid.....	530

	PAGE		PAGE
Nitric ether .....	530	Codein .....	617
Nitrous and sulphurous ethers .....	531	Strychnin and brucin .....	617
Boracic and silicic ethers .....	532	Caffein or thein .....	618
Carbonic ethers, urethan .....	533	Nicotin .....	618
Oxalic ethers, oxamic ether .....	534	Conicin .....	620
Mucic ether .....	535	Quinolein or leucole .....	620
Sulphocarbovinic or xanthic acid .....	536	Anilin or kyanole .....	621
Chlorohydric ether .....	536	Ethylammonia .....	622
Bromo, iodo, and cyanohydric ethers .....	537	Methylammonia .....	623
Sulphydric ethers .....	538	Amylammonia .....	624
Mercaptan .....	539	NEUTRAL SUBSTANCES IN PLANTS .....	625
<i>Oxidation of alcohol and ether</i> .....	541	Piperin, picrotoxin, cantharidin .....	626
Aldehyde .....	541	Asparagin, aspartic acid .....	627
Acetic acid .....	542	Phloridzin, glycyrrhizin .....	628
Manufacture of vinegar .....	543	NITRILS .....	629
Pyroligneous acid .....	545	Cyanogen, products of .....	630
Acetates .....	546	“ oxacids of .....	631
Acetic ether .....	548	“ fulminic acid .....	632
Acetone .....	549	“ sulphocyanides .....	633
Mesitylen .....	550	ESSENTIAL OILS .....	634
Cacodyl, alcarsin .....	551	Oil of turpentine or terebenthen .....	635
Chlorinated chlorohydric ether .....	554	Camphilen, terebilen, tereben .....	637
Chlorinated ether .....	558	Oils of lemon, orange, etc. ....	638
Chloral .....	561	Camphor, Japan .....	639
Chloracetic acid .....	563	“ Borneo .....	640
Chlorinated compound ethers .....	564	Menthen, cedren, etc. ....	641
Table of alcoholic compounds by sub-		<i>Benzoic Series</i> .....	641
stitution .....	566	Oil of bitter almonds .....	642
Ethyl theory (note) .....	568	Benzamide .....	643
<i>Lactic and butyric fermentations</i> .....	569	Benzoic acid .....	644
Lactic acid .....	573	“ ethers .....	645
Butyric acid, butyramide .....	574	Sulpho-nitrobenzoic acids .....	646
<i>Methylic alcohol, wood-spirit</i> .....	575	Benzoïn, benzil, benzin .....	648
Methylic ether .....	576	Benzone, amygdalin .....	650
Methylsulphuric ether .....	577	Emulsin, synaptase .....	651
Compound methylic ethers .....	578	<i>Salicin</i> .....	652
Marsh-gas .....	582	Saligenin .....	653
Formic acid .....	583	Salicylous acid, oil of spiræa .....	654
Methylal .....	585	Salicylic acid and ether .....	656
Chlorinated methylchlorohydric ether .....	585	Oil of wintergreen .....	656
Chloroform .....	586	<i>Oil of Cinnamon</i> .....	658
Bromo, iodo, sulfoform .....	588	Cinnamic acid, cinnamen .....	659
Chlorinated methylic ether .....	588	Balsams of Peru and Tolu .....	660
Table of methylic compounds by sub-		<i>Coumarin</i> .....	661
stitution .....	591	<i>Oil of Aniseed</i> , anisic acid .....	662
Methyl .....	593	Anisen, toluidin .....	663
ACIDS EXISTING IN PLANTS .....	594	<i>Oil of Cumin</i> , cuminic acid, cymen .....	664
Oxalic acid .....	594	<i>Oil of Cloves</i> , eugenic acid .....	665
Malic acid .....	595	<i>Amylic Alcohol</i> .....	665
Equisetic and fumaric acids .....	596	Amylin .....	666
Citric acid .....	596	Amylic ethers .....	667
Aconitic acid .....	597	Valerianic acid .....	669
Tartaric acid .....	598	<i>Enanthic Acid</i> .....	670
Tartar emetic .....	600	<i>Caoutchouc</i> .....	671
Action of heat on tartaric acid .....	601	Gutta-percha .....	673
Racemic acid .....	603	Resins .....	673
Tannic acid .....	605	Pimaric acid .....	674
Gallie acid .....	607	<i>Oil of Garlic</i> , allyl .....	675
Ellagic or bezoaric acid .....	609	Oil of mustard .....	676
Meconic acid .....	609	Thiosinnamin .....	676
Chelidonic acid .....	611	Myronic acid .....	677
Quinic acid, quinone .....	611	PRODUCTS OF DRY DISTILLATION .....	678
ORGANIC ALKALOIDS .....	612	Naphthalin .....	678
Quinin .....	613	Paraffin .....	681
Cinchonin .....	614	Phenic or carbolic acid .....	682
Morphin .....	615	Creasote .....	683
Narcotin .....	616	Naphtha .....	683

## TABLE OF CONTENTS.

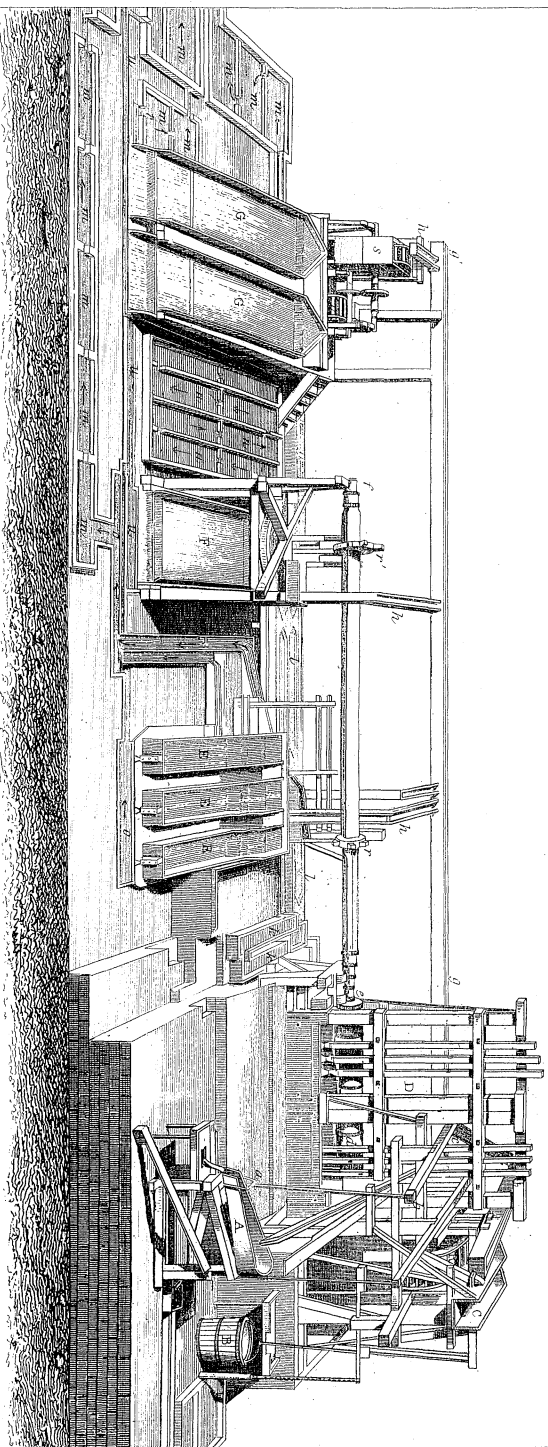
7

	PAGE		PAGE
FATS.....	684	Blood hematosin.....	740
Glycerin.....	689	“ coagulum.....	741
Stearic acid, stearic candles.....	690	“ analysis of.....	742
Margaric acid.....	692	Lymph.....	743
Oleic acid.....	693	Saliva, gastric juice.....	744
Action of sulphuric on the fat acids..	694	Bile.....	745
“ nitric “ “ ..	695	“ cholic acid.....	746
Succinic and adipic acids.....	697	Biliary calculi and cholesterin.....	747
Suberic and sebacic acids.....	698	Pancreatic and intestinal juice .....	747
Caproic, caprylic, and capric acids ...	699	Chyle and milk.....	748
Palm-oil, castor-oil.....	700	Lactometry.....	750
Spermaceti, ethal.....	701	Sugar of milk.....	751
Wax, cerin, myricin.....	703	Casein.....	752
ORGANIC COLOURING MATTERS.....	704	Making butter.....	752
Madder.....	705	Making cheese.....	753
Logwood.....	706	Excretions.....	754
Saffron, Quercitron, etc.....	707	Urine.....	754
Euxanthic acid.....	708	Urea.....	755
Carotin.....	709	Uric acid and derivatives.....	757
Chlorophyll.....	709	Hippuric acid.....	760
Cochineal.....	710	Urine, analysis of.....	761
Lichens.....	710	Urinary calculi.....	762
Indigo.....	712	Sweat.....	763
White indigo.....	714	Excrements.....	763
Isatin.....	715	Intestinal gases.....	763
ACTION OF PLANTS ON THE ATMOSPHERE	716	TECHNICAL ORGANIC CHEMISTRY.....	763
ANIMAL CHEMISTRY.....	719	Manufacture of bread.....	764
Bone.....	721	Brewing.....	766
Teeth, cartilage, horn.....	722	Cider and perry.....	768
Hair, skin, muscular tissue .....	723	Wine-making.....	769
Fibrin, creatin.....	724	Manufacture of beet-sugar.....	771
Inosic acid.....	725	“ cane-sugar .....	773
Gelatin, glue.....	726	Sugar-refining.....	775
Ichthyocolla, glycocoll.....	727	Manufacture of bone-black.....	777
Cerebral substance.....	728	Soap-boiling.....	778
Nutrition.....	729	Principles of dyeing.....	781
Digestion.....	730	Mordants.....	785
Blood, circulation of the .....	732	Calico printing.....	787
Respiration and animal heat.....	734	Tanning.....	788
Secretions.....	738	Charring wood and coal.....	790
Blood.....	738	Manufacture of illuminating gas.....	792
“ globules.....	739		





# GENERAL VIEW OF STAMPING & WASHING ORES



F. Water-wheel, giving movement to the whole machinery, & receiving water from the trough C.

e.d. Shaft of the water-wheel, provided with cams for raising the stamps D.

D. Two sets of stamps, one for coarse, the other for fine sludge. The water from the stamps containing fine matter in suspension, deposits the sand in the reservoirs, k, from which it passes through a series of canals & basins, l, n, where it successively deposits the finer matter suspended in it.

A. Sluicing stage, for assorting the sizes of ore, moved by the arms, a, b, h, c.

B. Lifting machine, moved by hand, but in more modern establishments by machinery.

E, E, E. Deposit troughs for washing coarse sludges, which empty their muddy waters through the troughs o, a into the basins m, n.

F. Sluicing table, moved by the small cam-wheel, c, on the main shaft of the water-wheel. The waters from it pass through the troughs u, u into the deposit basins m, n.

G, G. Sluicing tables. The sludge is stirred up in the water by the small dash-wheel v, moved by the small wheel s; & the muddy waters pass through the trough u.

into the deposit reservoirs, m, n.

g, g. Trough for conveying water through the whole establishment, distributing it through the spouts h, h.

The receiving basins m, n, into which the muddy waters flow constitute a kind of labyrinth of great extent, but the muddy waters from different parts of the establishment entering the basins at different points, the same part of the basins contains the same kind of deposit. The waters in passing from the labyrinth enter large reservoirs outside of the works, where they gradually deposit all the matters they hold in suspension.



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## TABLE OF CONTENTS OF VOL. II.

	PAGE		PAGE
PREPARATION OF ORES.....	9	IRON, composition of bar and cast-iron,	
Washing.....	10	and steel.....	116
Crushing by cylinders.....	11	CHROMIUM, oxides of.....	118
Swing-sieve.....	15	“ chromic acid.....	122
Jigging-machine.....	16	“ salts of.....	123
Stamping ore.....	17	“ chromates.....	125
Deposit-trough.....	18	“ analytic determination of...	128
Sleeping-table, or nicking-buddle.....	19	COBALT, metal and oxides.....	130
Percussion-table, or brake-table.....	20	“ salts of.....	131
MANGANESE.....	23	“ arsenical ores.....	132
“ oxides of.....	23	“ analytic determination of.....	133
“ acids of.....	25	“ <i>smalt and saffre</i> .....	134
“ salts of.....	28	“ Thenard's blue.....	135
“ sulphide and chloride of.....	29	NICKEL, metal and oxides of.....	136
“ analytic determination of.....	31	“ salts of.....	137
IRON, metallic.....	36	“ German silver.....	138
“ oxides of.....	40	“ analytic determination of.....	139
“ salts of.....	44	ZINC, distillation of.....	141
“ sulphide of.....	47	“ oxide of.....	142
“ chloride of.....	49	“ salts of.....	143
“ cyanides of.....	50	“ sulphide and chloride of.....	144
“ carburet of, cast-iron.....	53	“ analytic determination of.....	144
“ analytic determination of.....	54	“ <i>metallurgy of</i> .....	146
“ ores of.....	59	“ “ in Belgium.....	147
“ reduction of its ores, by the Cata-		“ “ in Silesia.....	150
lonian forge.....	61	“ “ in England.....	151
<i>Reduction in the blast-furnace</i> .....	66	CADMIUM, compounds of.....	153
“ the blast.....	67	“ analytic determination of.....	154
“ mixing ores.....	70	TIN.....	156
“ blowing the furnace.....	71	“ oxides of.....	158
“ hot-blast.....	77	“ salts of.....	160
“ waste-heat of blast-furnace.....	78	“ sulphides of.....	161
“ remelting pig-metal.....	80	“ chlorides of.....	162
“ conversion of cast into bar-iron....	82	“ behaviour of salts of.....	164
“ refining on the forge-hearth.....	83	“ <i>metallurgy of</i> .....	166
“ “ by puddling.....	87	TITANIUM.....	169
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“ Making sheet and tin plate.....	99	“ chlorides of.....	171
“ wire-drawing.....	101	COLUMBIUM, NIOBIUM, PELUPIUM, IL-	
“ making steel.....	102	MENIUM.....	174
“ “ forge steel.....	103	LEAD.....	174
“ “ blistered and cast-steel...	104	“ oxides of, litharge.....	175
“ tempering steel.....	107	“ red, or minium.....	178
“ dry assay of iron-ores.....	108	“ salts of.....	179
“ analysis of cast, and steel.....	111	“ acetates of, sugar of lead.....	183

	PAGE		PAGE
LEAD, carbonate of, white-lead.....	184	MERCURY, chlorides of, calomel.....	282
“ behaviour of salts of.....	186	“ “ corrosive subli- mate.....	284
“ sulphide of.....	186	“ “ white precipitate.....	285
“ chloride of.....	188	“ iodides of.....	286
“ analytic determination of.....	188	“ cyanide of.....	287
“ alloys, type-metal, and soft solder.....	189	“ analytic determination of.....	288
“ metallurgy of.....	190	“ amalgams of, mirrors.....	289
“ “ reduction by iron....	192	“ metallurgy of, in Idria.....	290
“ “ reverberatory pro- cess.....	196	“ “ at Almaden... ..	291
“ “ Scotch hearth.....	198	SILVER.....	293
“ “ cupellation.....	198	“ oxides of.....	294
“ “ Pattinson's process..	202	“ fulminating.....	295
“ making sheet, and pipe.....	202	“ salts of.....	296
“ casting shot.....	203	“ “ lunar caustic.....	297
BISMUTH.....	204	“ sulphides of.....	300
“ oxides of.....	205	“ chlorides of.....	301
“ salts of, pearl-white.....	206	“ analytic determination of.....	303
“ alloys of, fusible metal.....	208	“ metallurgy of.....	304
“ analytic determination of.....	208	“ “ Freiberg process..	305
“ metallurgy of.....	209	“ “ Mansfeld “.....	309
ANTIMONY.....	211	“ “ American “.....	310
“ oxides and acids of.....	212	“ alloys of.....	311
“ salts of.....	214	“ “ coin and plate.....	312
“ sulphides of, Kermes mineral.....	215	“ assay of alloys of, by cupella- tion.....	313
“ chlorides of.....	217	“ assay of alloys of, in the wet way.....	316
“ behaviour of salts of.....	218	“ assay of ores of.....	321
“ analytic determination of.....	219	GOLD and its compounds.....	322
“ detection of, in poisoning.....	221	“ purple of Cassius.....	325
“ alloys of.....	221	“ analytic determination of.....	326
“ metallurgy of.....	222	“ metallurgy of.....	326
URANIUM, and its oxides.....	224	“ “ Tyrolese bowls.....	328
“ salts of.....	225	“ alloys of.....	329
“ analytic determination of.....	228	“ separation of, and silver, by sul- phuric acid.....	329
TUNGSTEN, and its oxides.....	230	“ separation of, and silver, by ni- tric acid.....	331
“ analytic determination of.....	232	“ gilding and silvering.....	331
MOLYBDENUM, its oxides and salts.....	233	“ “ “ by immer- sion.....	332
VANADIUM.....	235	“ galvanic gilding.....	333
COPPER.....	236	“ “ silvering.....	334
“ oxides of.....	237	“ galvanoplastics.....	335
“ salts of.....	239	“ assay of alloys of, by quartation.....	336
“ “ blue vitriol.....	240	“ “ “ by the touch- needle.....	338
“ “ mineral and Scheele's green.....	242	PLATINUM.....	339
“ “ verdigris.....	243	“ black.....	340
“ sulphides of.....	243	“ flameless lamp.....	341
“ chlorides of.....	244	“ oxides of.....	342
“ analytic determination of.....	245	“ salts of.....	343
“ metallurgy of.....	247	“ chlorides of.....	345
“ “ Mansfeld process..	249	“ ammonia-bases of.....	346
“ “ eliquation of silver.....	251	“ analytic determination of.....	347
“ “ English process....	256	“ extraction of.....	349
“ alloys of, and zinc.....	263	OSMIUM.....	350
“ “ “ brass.....	264	“ compounds of.....	351
“ “ tin, bronze.....	265	“ extraction of.....	352
“ “ cannon-casting.....	266	IRIDIUM.....	353
“ “ tinning copper and brass.....	269	“ compounds of.....	354
“ analysis of brass and bronze.....	270	PALLADIUM, and its compounds.....	356
MERCURY.....	271	RHODIUM, and its compounds.....	358
“ purification of.....	272	RUTHENIUM.....	360
“ oxides of.....	273		
“ salts of.....	275		
“ fulminating.....	279		
“ amide-base of.....	279		
“ sulphides of, cinnabar.....	281		

## FOURTH PART.

## ORGANIC CHEMISTRY.

	PAGE		PAGE
INTRODUCTION.....	361-445	ESSENTIAL PROXIMATE PRINCIPLES OF	
Organized and organic bodies.....	362	PLANTS.....	446
Proximate analysis of organic sub-		<i>Cellulose</i> .....	446
stances.....	363	Lignin.....	449
<i>Ultimate analysis of organic sub-</i>		<i>Albuminous Vegetable Substances</i> .....	451
<i>stances</i> .....	366	Albumen.....	453
Ultimate analysis, determination of		Circular polarization (note).....	454
carbon and hydrogen.....	367	Gluten, vegetable fibrin, and casein...	460
Ultimate analysis, desiccation.....	369	<i>Amylaceous Substances</i> .....	461
“ “ combustion.....	371	Inulin and lichenin.....	467
“ “ of non-volatile li-		Gums, arabin, cerasin, bassorin.....	468
quids.....	374	<i>Sugar</i> .....	469
“ “ of volatile sub-		Cane-sugar.....	470
stances.....	375	Caramel, saccharic acid.....	471
“ “ of gaseous organic		Fruit-sugar.....	474
bodies.....	375	Grape-sugar.....	475
“ “ determination of		Glucic acid.....	476
carbonic acid by		Determination of sugar by oxide of cop-	
volume.....	377	per.....	477
“ “ determination of		Determination of sugar by polarization	478
nitrogen by vo-		<i>Gelatinous Principles</i> , pectose.....	478
lume.....	380	Pectin and pectic acid.....	479
Ultimate analysis, determination of		Table of pectic acids.....	483
nitrogen as ammonia.....	382	Mannite.....	484
Ultimate analysis, determination of		<i>Action of Acids on Lignin, Starch, and</i>	
sulphur.....	385	<i>Sugar</i> .....	485
Ultimate analysis, determination of		Dextrin.....	485
phosphorus.....	385	British gum.....	486
Ultimate analysis, determination of		Diastase.....	487
chlorine, bromine, iodine, and oxy-		Glucose, manufacture of.....	487
gen.....	386	Ulm and humin.....	489
<i>Construction of a formula for an organic</i>		Action of nitric acid, oxysaccharic	
substance.....	387	acid.....	491
“ “ when it is acid	387	Gun-cotton.....	491
“ “ from its mine-		Collodion.....	492
ral base.....	393	Mucic acid.....	493
“ “ when it is basic	397	<i>Spontaneous Decomposition of Plants</i> ...	494
“ “ when neither		Mineral fuel.....	494
acid nor basic	399	Varieties of coal.....	496
Determination of density of vapours.....	406	Analysis “.....	497
Simultaneous temperatures in thermo-		Tables of composition of coal....	500, 503
meters differently constructed.....	413	<i>Alcoholic Fermentation</i> .....	505
Air-thermometer (note).....	414	Yeast or ferment.....	507
<i>Analysis of gases</i> , apparatus for.....	422	Alcohol.....	511
“ “ absorbing reagents...	430	Alcoholometry.....	513
“ “ examples of.....	433	Sulphovinic acid.....	515
“ “ oxygen and nitrogen	433	Ether.....	516
Analysis of gases, oxygen, nitrogen,		Olefiant gas.....	520
and hydrogen.....	435	Ethionic acid.....	522
Analysis of gases, oxygen, nitrogen, and		Dutch liquid.....	523
carbonic oxide.....	436	Chlorinated olefiant gas.....	524
Analysis of gases, oxygen, carburetted		Oil of wine.....	528
hydrogen, etc.....	437	Ethers and vinic acids.....	529
Analysis of gases, complex mixtures....	443	Phosphovinic acid.....	530



	PAGE		PAGE
Nitric ether .....	530	Codein.....	617
Nitrous and sulphurous ethers .....	531	Strychnin and brucin.....	617
Boracic and silicic ethers.....	532	Caffeïn or theïn.....	618
Carbonic ethers, urethan.....	533	Nicotin.....	618
Oxalic ethers, oxamic ether.....	534	Conicin.....	620
Mucic ether.....	535	Quinoleïn or leucole.....	620
Sulphocarbovinic or xanthic acid.....	536	Anilin or kyanole.....	621
Chlorohydric ether.....	536	Ethylammonia.....	622
Bromo, iodo, and cyanohydric ethers.....	537	Methylammonia.....	623
Sulphydric ethers.....	538	Amylammonia.....	624
Mercaptan.....	539	NEUTRAL SUBSTANCES IN PLANTS.....	625
<i>Oxidation of alcohol and ether.....</i>	541	Piperin, picrotoxin, cantharidin.....	626
Aldehyde.....	541	Asparagin, aspartic acid.....	627
Acetic acid.....	542	Phloridzin, glycyrrhizin .....	628
Manufacture of vinegar.....	543	NITRILS.....	629
Pyroligneous acid.....	545	Cyanogen, products of.....	630
Acetates.....	546	“ oxacids of.....	631
Acetic ether.....	548	“ fulminic acid.....	632
Acetone.....	549	“ sulphocyanides.....	633
Mesitylen.....	550	ESSENTIAL OILS.....	634
Cacodyl, alcarsin.....	551	Oil of turpentine or terebenthen.....	635
Chlorinated chlorohydric ether.....	554	Camphilen, terebilen, tereben.....	637
Chlorinated ether.....	558	Oils of lemon, orange, etc.....	638
Chloral.....	561	Camphor, Japan.....	639
Chloracetic acid.....	563	“ Borneo.....	640
Chlorinated compound ethers.....	564	Menthen, cedren, etc.....	641
Table of alcoholic compounds by sub-		<i>Benzoic Series</i> .....	641
stitution.....	566	Oil of bitter almonds.....	642
Ethyl theory (note).....	568	Benzamide.....	643
<i>Lactic and butyric fermentations.....</i>	569	Benzoic acid.....	644
Lactic acid.....	573	“ ethers.....	645
Butyric acid, butyramide.....	574	Sulpho-nitrobenzoic acids.....	646
<i>Methylic alcohol, wood-spirit .....</i>	575	Benzoïn, benzil, benzin.....	648
Methylic ether.....	576	Benzone, amygdalin.....	650
Methylsulphuric ether.....	577	Emulsin, synaptase.....	651
Compound methylic ethers.....	578	<i>Salicin</i> .....	652
Marsh-gas.....	582	Saligenin.....	653
Formic acid.....	583	Salicylous acid, oil of spiræa.....	654
Methylal.....	585	Salicylic acid and ether.....	656
Chlorinated methylechlorohydric ether.....	585	Oil of wintergreen.....	656
Chloroform.....	586	<i>Oil of Cinnamon</i> .....	658
Bromo, iodo, sulphoform.....	588	Cinnamic acid, cinnamen.....	659
Chlorinated methylic ether.....	588	Balsams of Peru and Tolu.....	660
Table of methylic compounds by sub-		<i>Coumarin</i> .....	661
stitution.....	591	<i>Oil of Aniseed</i> , anisic acid.....	662
Methyl.....	593	Anisen, toluidin.....	663
ACIDS EXISTING IN PLANTS.....	594	<i>Oil of Cumin</i> , cuminic acid, cymen .....	664
Oxalic acid.....	594	<i>Oil of Cloves</i> , eugenic acid.....	665
Malic acid.....	595	<i>Amylic Alcohol</i> .....	665
Equisetic and fumaric acids.....	596	Amylin.....	666
Citric acid.....	596	Amylic ethers.....	667
Aconitic acid.....	597	Valerianic acid.....	669
Tartaric acid.....	598	<i>Enanthic Acid</i> .....	670
Tartar emetic.....	600	<i>Cuoutchoue</i> .....	671
Action of heat on tartaric acid.....	601	Gutta-percha.....	673
Racemic acid.....	603	Resins.....	673
Tannic acid.....	605	Pimaric acid.....	674
Gallie acid.....	607	<i>Oil of Garlic</i> , allyl.....	675
Ellagic or bezoaric acid.....	609	Oil of mustard.....	676
Meconic acid.....	609	Thiosinamin.....	676
Chelidonic acid.....	611	Myronic acid.....	677
Quinic acid, quinone.....	611	PRODUCTS OF DRY DISTILLATION.....	678
ORGANIC ALKALOIDS.....	612	Naphthalin.....	678
Quinin.....	613	Paraffin.....	681
Cinchonin.....	614	Phenic or carbohic acid.....	682
Morphin.....	615	Creasote.....	683
Narcotin.....	616	Naphtha.....	683

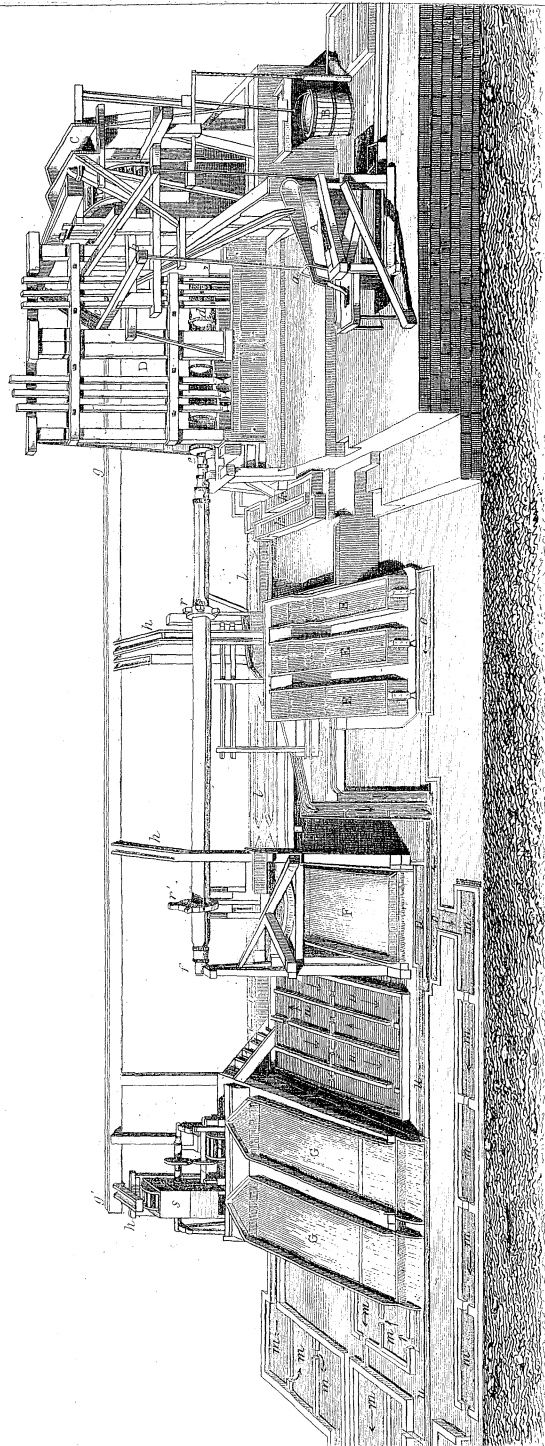
## TABLE OF CONTENTS.

7

	PAGE		PAGE
FATS.....	684	Blood hematosin.....	740
Glycerin.....	689	“ coagulum.....	741
Stearic acid, stearic candles.....	690	“ analysis of.....	742
Margaric acid.....	692	Lymph.....	743
Oleic acid.....	693	Saliva, gastric juice.....	744
Action of sulphuric on the fat acids..	694	Bile.....	745
“ nitric “ “ ..	695	“ cholic acid.....	746
Succinic and adipic acids.....	697	Biliary calculi and cholesterin.....	747
Suberic and sebacic acids.....	698	Pancreatic and intestinal juice.....	747
Caproic, caprylic, and capric acids ...	699	Chyle and milk.....	748
Palm-oil, castor-oil.....	700	Lactometry.....	750
Spermaceti, ethal.....	701	Sugar of milk.....	751
Wax, cerin, myricin.....	703	Casein.....	752
ORGANIC COLOURING MATTERS.....	704	Making butter.....	752
Madder.....	705	Making cheese.....	753
Logwood.....	706	<i>Excretions</i> .....	754
Saffron, Quercitron, etc.....	707	Urine.....	754
Euxanthic acid.....	708	Urea.....	755
Carotin.....	709	Uric acid and derivatives.....	757
Chlorophyll.....	709	Hippuric acid.....	760
Cochineal.....	710	Urine, analysis of.....	761
Lichens.....	710	Urinary calculi.....	762
Indigo.....	712	Sweat.....	763
White indigo.....	714	Excrements.....	763
Isatin.....	715	Intestinal gases.....	763
ACTION OF PLANTS ON THE ATMOSPHERE	716	TECHNICAL ORGANIC CHEMISTRY.....	763
ANIMAL CHEMISTRY.....	719	Manufacture of bread.....	764
Bone.....	721	Brewing.....	766
Teeth, cartilage, horn.....	722	Cider and perry.....	768
Hair, skin, muscular tissue.....	723	Wine-making.....	769
Fibrin, creatin.....	724	Manufacture of beet-sugar.....	771
Inosic acid.....	725	“ cane-sugar.....	773
Gelatin, glue.....	726	Sugar-refining.....	775
Ichthyocolla, glyccocoll.....	727	Manufacture of bone-black.....	777
Cerebral substance.....	728	Soap-boiling.....	778
Nutrition.....	729	Principles of dyeing.....	781
Digestion.....	730	Mordants.....	785
Blood, circulation of the.....	732	Calico printing.....	787
Respiration and animal heat.....	734	Tanning.....	788
<i>Secretions</i> .....	738	Charring wood and coal.....	790
Blood.....	738	Manufacture of illuminating gas.....	792
“ globules.....	739		



# GENERAL VIEW OF STAMPING & WASHING ORES



R. Water-wheel, driving movement to the whole machinery, & moving water from the trough C.  
 a. d. Shaft of the water wheel, provided with cams for raising the stamps D.  
 D. Two sets of stamps, one for coarse, the other for fine sludge. The water from the stamps containing fine matter in suspension, deposits the sand in the reservoirs k. k. from which it passes through a series of canals & basins U. n. n. where it successively deposits the finer matter suspended in it.  
 A. Sliding sieve, for assorting the sizes of ore, moved by the arms, a. b. c.

B. Trough for conveying water through the whole establishment, distributing it through the spouts, h. h.  
 The receiving basins m. m. into which the muddy waters flow constitute a kind of labyrinth of great extent, but the muddy waters from different parts of the establishment entering the basins at different points, the same part of the basins contains the same kind of deposit.  
 The waters in passing from the labyrinth enter large reservoirs outside of the works, where they gradually deposit all the matters they hold in suspension.

into the deposit reservoirs, m. m.  
 g. g. Trough for conveying water through the whole establishment, distributing it through the spouts, h. h.  
 The receiving basins m. m. into which the muddy waters flow constitute a kind of labyrinth of great extent, but the muddy waters from different parts of the establishment entering the basins at different points, the same part of the basins contains the same kind of deposit.  
 The waters in passing from the labyrinth enter large reservoirs outside of the works, where they gradually deposit all the matters they hold in suspension.



# ELEMENTS OF CHEMISTRY.

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## THIRD PART.

§ 732. ALTHOUGH the metals described in the second part of this work are never technically employed in the metallic state, they still find very extensive application in the state of various compounds, all of which are manufactured in chemical works by processes similar to those employed for obtaining them in the laboratory on a smaller scale.

Among the metals yet remaining for our examination, however, a considerable number are employed in the metallic state, and are extracted from their ores by processes of a particular kind, called *metallurgical processes*. In every case when they are to be used in the metallic state they must fulfil all the conditions enumerated (§ 276); which, however, many do not, as some are of rare occurrence, while the extracting of others presents too great practical difficulties, and still others have as yet found no technical application, being, therefore, of purely scientific interest. Nevertheless, on account of the great analogy existing between them in a chemical point of view, the study of those which find a technical application cannot be separated from that of those which are not so applied. The latter will, therefore, occupy our attention as well as the former, but to a much more limited extent.

---

### MECHANICAL PREPARATION OF ORES.

§ 733. Under the general name of *ores* are comprised such combinations of metals, occurring in nature, as contain a sufficient proportion of metal to be worked with profit. The proportion varies with the marketable value of the metal, and according to the greater or less facility with which it can be obtained from its combination in the ore: iron ores, for instance, the commercial price of which metal is very low, must therefore be very rich if they are to be profitably worked. The poorest minerals from which iron

could be extracted must contain at least 25 per cent. of iron ; and the metal must moreover exist in them in a state from which it can be easily reduced, in order to be iron *ores*. A mineral of frequent occurrence is *iron pyrites*, a combination of iron with sulphur, which contains about 47 per cent. of the former, but still cannot be considered as an ore, as the treatment to which it must be subjected in order to obtain a good quality of iron would be far too costly. Copper, on the contrary, the commercial value of which is much higher than that of iron, can be extracted with advantage from ores containing only a few per cent. of the metal, even if these be in combination with sulphur ; and ores which contain only some thousandths of silver or of gold can be worked to advantage.

§ 734. An ore, of whatever kind it may be, is seldom sufficiently rich to be at once subjected to metallurgical processes, but is, in general, worked with greater advantage after having been sorted, and prepared by various mechanical operations, which tend to separate from them the greater part of the earthy substances, technically termed *gangue*, with which they were mixed. The larger pieces of the gangue are usually separated from the ore in the mine itself, and used to fill up the excavations already made in the rock ; so that only such fragments are taken out of the mine as can be advantageously prepared for smelting by mechanical operations.

§ 735. The ores of iron employed are always very rich, as those which are not so have not sufficient value to be made richer by costly mechanical processes ; in general, therefore, the argillaceous parts are merely separated by washing (*débouillage*).\* Sometimes the ore is left exposed to the atmosphere for several months, as the clay is thus rendered more friable and more easily detached. The washing of iron ores is performed (in France) in the middle of a stream of water, in a series of apparatus called *patouillets*. It is sometimes considered sufficient to turn and stir the ore in the stream with a spade, by which the argillaceous parts are detached and carried away ; but the shaking up of the ore is more frequently effected by means of a small water-wheel R (fig. 461), set in motion by the stream. The ore, thrown with a spade into the long trough A, where the water running over it frees it from a part of its clay, is thence transferred to the semi-cylindrical box B, which is filled with water, where it is stirred by iron arms attached to the axle of the water-wheel. The muddy water runs off by an outlet at the top of the box, and the washed ore, which is taken out through the orifice *o* in the lower part of the box, falls into the trough D,

---

\* Since hard ores are more abundant than soft in the United States, the poorer clayey ores, instead of being enriched by any mechanical process, are usually sought after to mix with the harder ores and render them more easy of fluxion in the furnace.—*J. C. B.*

whence the workman removes it when he finds it to be sufficiently washed.

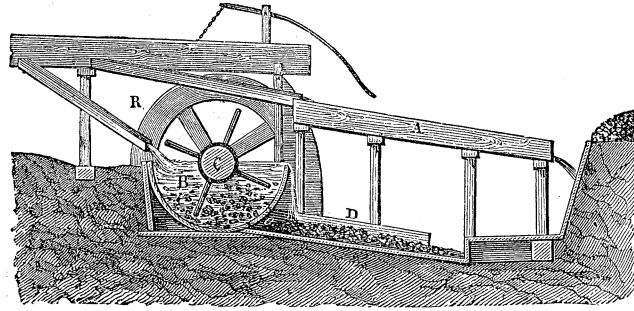


Fig. 461.

§ 736. The ores of other metals, when taken from the mine, are generally sorted by the hands of females and children, who separate them into—1st, pieces rich enough to be immediately sent to the smelting-works; 2dly, fragments composed of ore and gangue, which must be subjected to mechanical preparations; and 3dly, pieces of gangue, which are thrown aside as useless. Let us now examine the mechanical operations to which the second class is subjected. When the metalliferous mineral is so intimately mixed with the gangue that it cannot be separated by the hammer, the pieces are reduced to a small size between cast-iron cylinders or under stampers. Fig. 462 represents an apparatus of crushing-cylinders, and figs. 463 and 464 show the arrangement of the cylinders. Two kinds of hard cast-iron cylinders are employed; fluted (fig. 464), and smooth ones (fig. 463); in the former of which the large fragments are broken, while the smooth cylinders reduce the pieces furnished by them to a still smaller size.

Only one of these cylinders, A, receives motion from the water-wheel, the desired velocity being given to it by a system of cogs, while the second cylinder B is moved by the former. The cylinder A is borne by two fixed uprights K, while the supports L of B are movable on the sliding-boards *ab*, *cd*. The cylinder B therefore moves away from A whenever a piece presents itself which would oppose too much resistance to crushing; but at other times, it is kept pressed against A by the weight P, suspended to the extremity of a long lever ST.

The ore is brought to the crushing machine by cars, moving on a railroad FF'. The workman throws it with a spade into a wooden hopper U placed above the cylinders; and when it is reduced in size by passing between them, it falls on an inclined jolting-box M, the bottom of which consists of a wire sieve, with very small openings at the top, and larger ones at the lower part. The finest



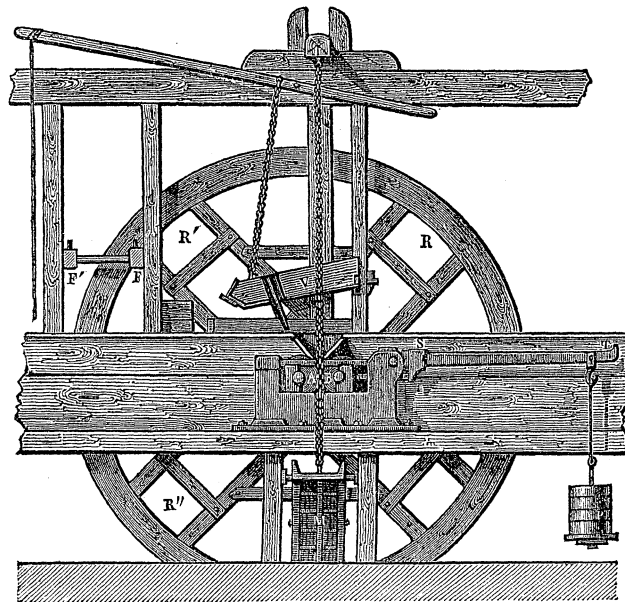


Fig. 462.

grains pass through the upper sieves; while those fragments which have passed the under ones roll to the bottom of the box M, and fall into a wheel RR'R'', provided with boxes; which, by a slow rotary movement, brings the pieces of ore up again into the box U,

Fig. 463.

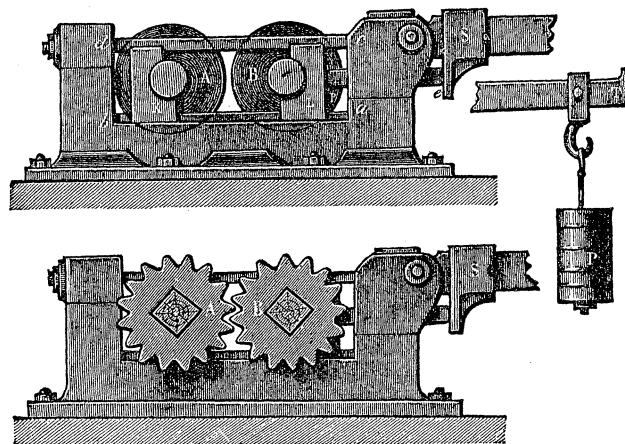


Fig. 464.

whence they again pass between the cylinders with the ore recently supplied from the mine.

The ore, when broken by the fluted cylinders, is thus sorted by the sieves in the box M into different sized grains, from the heaps of which the largest pieces are often removed by hand; then such portions are separated as are fit for immediate smelting, the pieces of gangue are thrown aside, and the mixture of ore and gangue which requires again to be reduced in size is passed through the system of smooth cylinders. In this case the ore is not thrown directly into the box U, but into a box V divided into different parts (fig. 462), the bottom of which consists of a sieve, which, keeping back the too large fragments, allows only those of the proper dimensions to fall on the cylinders. The crushed ore is again received in a box M, the sieves of which are much finer than those which receive the pieces falling from the fluted cylinders. By this operation pieces of 4 or 5 millimetres (about  $\frac{1}{8}$  inch) are obtained, which is a convenient size for the subsequent operations. The forming of smaller pieces and of dust cannot entirely be avoided, although it is sought to diminish their quantity as much as possible.

§ 737. The ore, reduced to more or less fine grains, is submitted to further operations in the *jigging machine*, (*crible à dépôt*,) the theoretical principles of which are the following:

If bodies differing in shape, size, and specific gravity be let fall into a liquid which is quiet at the time, these bodies will experience different resistances in their fall, and arrive at different times at the bottom of the liquid; so that a kind of separation is effected, during their fall, by the position the pieces occupy in the deposit formed at the bottom of the vessel.

If we suppose these bodies to be similar as to shape and size, but differing in their specific gravity, then they will all experience equal loss in the totality of their movement in the liquid, because the resistance a body meets with in passing through a liquid, depends entirely on its form and extent of surface, but not on its density. But the loss will be more sensible as the momentum of the bodies is greater, that is, as their specific gravity is higher; so that the least dense particles, traversing the central strata of the liquid more slowly than the others, will arrive last at the lower part of the vessel; and the deposit formed will thus consist of different layers, in which the particles will have arranged themselves according to their specific gravities, the most dense occupying the lowest place and the lightest ones the top.

Supposing, on the other hand, the bodies falling into the liquid to be all of equal density, and, moreover, all to have the same form,—for example, to be all cubes or spheres,—but differing in size, then will their momentum during their fall be in proportion to their volume. The resistance opposed to the particles by the liquid will

be proportioned to their surfaces, as we have supposed both their form and relative position while passing through the liquid to be the same. Therefore, since volumes vary as the cubes of homologous dimensions, while surfaces only vary as the squares of such dimensions, the momenta of the bodies will stand in proportion to the cubes  $d^3$  of one of their dimensions, while the resistance offered to them by the liquid will be proportional only to the squares  $d^2$  of the same dimension. If  $M$  and  $m$  represent the volumes of two bodies of the same density, and  $D$  and  $d$  their homologous dimensions, then will their momenta be proportional to  $Mg$  and  $mg$ , or to  $D^3\delta g$  and  $d^3\delta g$ ;  $\delta$  representing the specific gravities of the bodies, and  $g$  their absolute weight. The loss of momentum they experience by the resistance of the liquid will be proportional to  $D^2$  and  $d^2$ ; and is a fractional part of the whole momentum, larger for the smaller bodies than for those of a larger size, this fraction being  $\frac{aD^2}{D^3\delta g}$  or  $\frac{a}{D\delta g}$  for the largest, and  $\frac{ad^2}{d^3\delta g}$  or  $\frac{a}{d\delta g}$  for the smallest, where  $a$  represents the coefficient of resistance, which is constant in both cases. The largest particle will therefore arrive first at the bottom of the liquid, and the deposit will consist of strata arranged according to the size of the pieces constituting them, the largest occupying the lowest situation.

Lastly, we will suppose the bodies to be equal as regards density and volume, but differing in form,—some for instance, being cubes, and others laminated rectangles; then will the latter, having a greater extent of surface than the cubes, meet with a greater resistance while traversing the liquid; and the cubes, arriving first at the bottom of the vessel, will leave the flattened particles in a layer on the upper surface of the deposit formed.

Let us now examine how these principles may be applied to the preparation of ores. We have seen that the sieves placed under the crushing-cylinders divide the material into equal classes, each of which is composed of pieces of a nearly uniform size; but we will now, to make the reasoning more simple, suppose these fragments, consisting of pure ore, or pure gangue, or a mixture of the two, to be exactly equal as to form and volume. Metalliferous ores being in general much heavier than the gangue by which they are accompanied, the fragments of the former will evidently first arrive at the bottom of the vessel, and on them the pieces composed of ore and gangue will deposit, while the fragments of pure gangue will constitute the uppermost layer. The deposit can then be divided into three parts: pure gangue, which lies uppermost, and is rejected; pure ore, forming the lowest stratum, which is sent to the smelting-works; and lastly, an intermediate layer, consisting of ore and gangue not sufficiently rich for immediate smelting, which must again be crushed, and undergo the process of washing over again.

It is evidently essential for the process of separation to obtain

the fragments as equal as possible, regarding both form and size ; but this condition cannot be fulfilled at will. By means of sieves of different fineness equality of size can be attained with more or less accuracy ; but by no known process can the pieces be obtained of a similar form, because this latter character depends on the molecular constitution of the minerals to be separated, on their cleavage, etc. It may therefore very well occur that a species of crushed ore may contain lamellar fragments of pure metalliferous ore, and cubic or spherical pieces of gangue, which nevertheless passed through the same sieve ; and that therefore the ore, which by virtue of its greater specific gravity tends to fall faster through the water than the gangue, will still form the upper layer of the deposit, on account of the greater resistance the liquid offers its lamellar fragments compared with that opposed to the cubic pieces of gangue. As all these circumstances present themselves simultaneously in practice, the separation of ores from their gangue is prevented from being as perfect as it would be if the simple cases just now supposed could be realized.

§ 738. The separation of ores into pieces of an equal size is of such importance, that it is frequently done with the pieces which have already been sorted by hand, or with the larger pieces from the crushing cylinders. Fig. 465 represents the swing-sieve (*crible à secousses*) employed for this purpose, which consists of two boxes

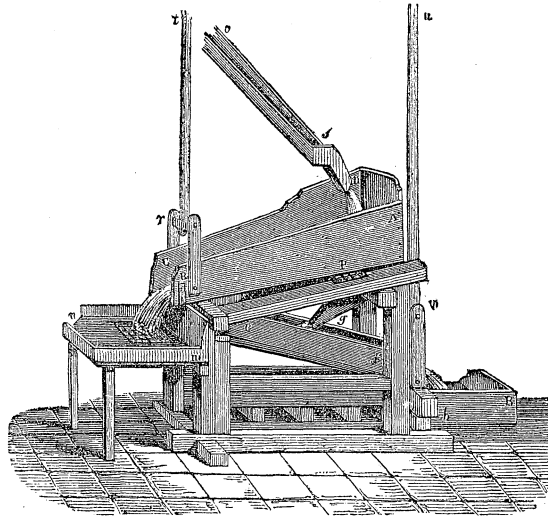


Fig. 465.

ABCD, *ef*, placed one above the other, both of which are kept in motion by the rods *tr* and *uv*, connected with a water-wheel. Part of the water led into the first box by means of the canal *os* passes,

by the canal *g*, into the box underneath; and the bottom of both boxes consists of a sieve, the meshes of which are larger in the box ABCD than in the other. A part of the ore which is placed in the upper sieve falls through into the sieve *ef*, where it is again sifted; and the ore is thus divided into grains of three different sizes. That which is too coarse to pass through the meshes of the sieve in ABCD falls on the platform *mn*, while the grains which remained on the sieve in *ef* are collected in the box *bR*, and lastly, the finest quality, which has escaped through the undermost sieve, is received by a box placed directly underneath the latter.

§ 739. A jigging machine (fig. 466) consists of a cylindrical box C, the bottom of which is a piece of wire-gauze or netting, with meshes of sufficient fineness to retain the fragments of ore. The

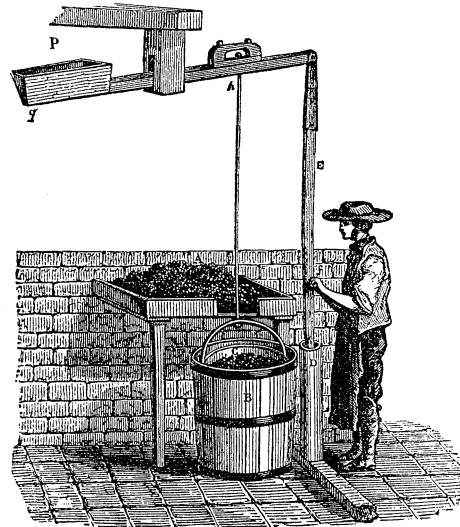


Fig. 466.

sieve is suspended by an iron bar *h*, attached to a horizontal bar *qh*, and counterbalanced by the weight *P*; and is kept in a tub *B*, which is filled with water. The workman sets the machine in motion by means of a vertical wooden pole *E*, which is guided by moving in the slider *D*. Taking the ore to be washed from the table *A*, he half-fills the sieve *C*, and then keeps the latter in a lively jolting motion in the water. The sieve receives during its descent a violent concussion against the bottom of the tub, when the water, penetrating through the

sieve, holds in suspension the ore, which by the shock is for a moment not influenced by its own weight; and the different pieces which fall back from the centre of the liquid have a tendency to separate, according to the laws developed above. When the height of the fall is small, a numerous repetition of shocks has the same effect in separating the pieces as when they fall from a greater height. The workman then, after some time, finds—1st, at the upper surface of his sieve, a layer of pure gangue, which can be thrown aside, or, at least, very poor ore, which must be stamped to powder in order to separate any parts that might be worth smelting; 2dly, a central stratum, consisting of fragments of ore and gangue com-

bined, which ought to be reduced in size before being again jigged; and 3dly, at the bottom of his sieve, a layer of ore of sufficient purity to be smelted. The central layer is generally set aside, and, when a sufficient quantity has been collected, is subjected to another jigging without being first reduced in size, by which he obtains again a quantity of ore fit for smelting.

In well-arranged works the jigging-machines are set in motion by water-power, in which case apparatus of a much larger size may be used, and may, moreover, be superintended by children.

By this process very small fragments of ore, of the diameter of 1 millimetre, may be purified; but the meshes of the wire-gauze in the jigging-machine must then be much finer than those employed for washing larger fragments.

§ 740. Such ores as cannot be sufficiently enriched by the use of sieves are sent to the stamping-mill (fig. 467), which is com-

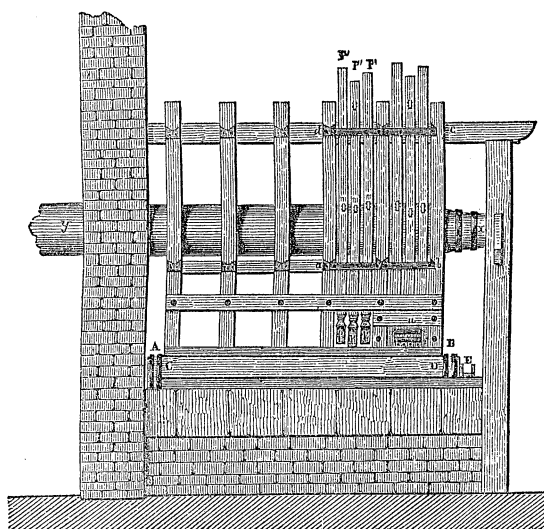


Fig. 467.

posed of a system of stampers  $PP'$ , consisting of pieces of timber  $P'$ , shod at the lower end by cast-iron pieces  $P$ . All the stampers fall into a single trough  $u$ , the bottom of which consists of a strong sheet-iron plate, sustained by a solid foundation of masonry, while its sides are made of iron sieves, or plates of sheet-iron pierced with holes. A water-wheel moves the axle  $xy$ , on the surface of which cams are fixed, which, by lifting the catches  $m$ , set the stampers in motion. (In the cut, the lateral walls of the trough are supposed to have been removed from before three of the stampers, in order to show the iron ends  $P$  of the latter.) The cams are so arranged on the axle  $xy$ , that by always lifting but one of the stampers at a time, the strain on the machinery is kept as constant as possible.

A current of water constantly flowing through the trough of the stamping-mill, into which ore is thrown with a spade, the parts which are already reduced to a sufficient fineness flow off through

the lateral sieves, being held in suspension by the water, from which they tend to deposit in the canals CD, E extending along the whole length of the battery of stampers. They are thence led in circuitous windings, called a *labyrinth*, over the floor of the building. The coarser particles are deposited at the heads of the various canals, while the fine grains are carried farther away; and as the waters, which traverse the channels at a very slow rate, are often still muddy after having passed through the whole system, they are conducted into large reservoirs, where they deposit even the finest particles they held in suspension. The deposit in the channels is called *sludge*, (schlich;) while that in the reservoirs, which resembles a thin mud, is termed *mud* or *fine sludge*, (schlamm:) the former differs in size of grain as well as in metallic richness, according to the different parts of the canals from which it is taken, and is thus divided into several classes, each of which is separately subjected to further operations.

The sludge is washed in three different kinds of apparatus: the *deposit-trough*, (caisse à tombeau,) the *sleeping-table* or *nicking-buddle*, (table dormante,) and the *percussion-table* or *brake-table*, (table à secousse.)

§ 741. The physical principles on which the washing of sludge is founded are rather different from those of the washing in sieves, as the latter is applicable only to fragments of a certain size. The ore no longer acts by its weight in a quiet liquid, but is in this case submitted to the action of running water on an inclined plane. The impulse imparted to the different pieces by the water being now proportional to their surfaces, but independent of their volumes and densities, they would, were their surfaces equal, be carried more or less far by the impulse of the liquid, according to their weight; and, if their form were similar at the same time, those of the least specific gravity would be carried farthest. But if their densities and volumes were equal, those presenting the greatest extent of surface would be deposited farthest off; and lastly, with equal densities and forms, the smaller particles would go farther than the larger ones, because they present the greater relative extent of surface. We see, therefore, that in these new operations, as well as in washing with sieves, the separation of the ore depends not only on the specific gravities, but also on the volumes and forms of the small pieces; for which reason, the ore to be washed must be of as equal a grain as possible.

§ 742. The *deposit-trough* consists of long wooden troughs BC (fig. 468), the bottoms of which are slightly inclined, and closed at their extremity C by a board pierced with several holes at different heights, which are closed with stoppers during the operation. The sludge to be washed is placed on the benches A at the head of the machine, where it is met by a current of water, which, taking the ore into suspension, falls into the boxes BC, and there deposits it

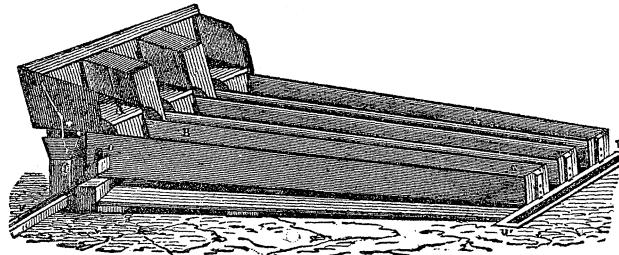


Fig. 468.

again at different distances from the bench A, while the finest particles still remain in the water and render it muddy. As soon as the boxes are filled with water, the supplying stream is turned off, and the openings at the extremity C are uncorked; the muddy water, then running through the canal UU' and a system of troughs into reservoirs, there deposits the particles it carried away. The washing of a fresh quantity of ore is then begun immediately, the sludge and mud of which is again borne by the water to the reservoirs and there deposited; and so on until the deposit has attained the thickness of a foot or two; each operation differing from the former only in the manner in which the water is let off through C, as each time a higher opening is unplugged.

The deposit of ore in the bottom of the box AB is divided into three parts, which are treated separately in the subsequent operations. The sludge on the highest part of the inclined is often rich enough to be sent to the furnaces at once; while the deposit on the centre and lowest part, the latter of which is the poorest, are subjected to new washings, either in the machine just described or on the percussion or the sleeping-tables.

§ 743. The *sleeping-tables* (sometimes, called in the French, *tables jumelles*, from their being generally arranged in pairs) consist of inclined tables AB (fig. 469), from 20 to 24 feet long, furnished with borders of wood, serving to keep the water running over them in

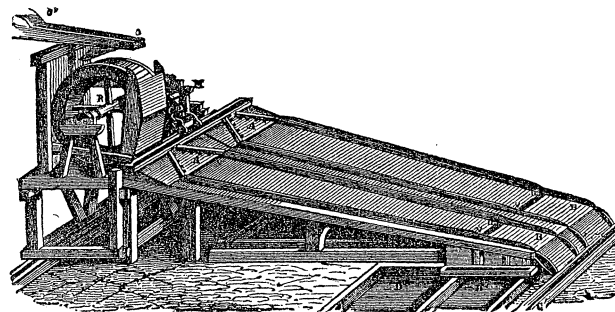


Fig. 469.



its place. At the head A of the table, two laths are set at the angle BAC (fig. 470), on a plane which is more inclined than the

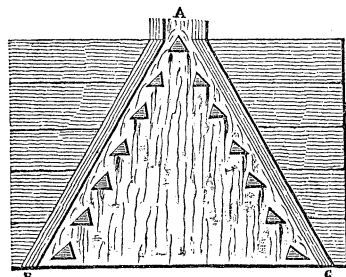


Fig. 470.

long plane; and between which only a small aperture A is left, through which the water with suspended sludge is introduced. Small triangular prisms of wood, set up on this inclined plane, equally divide the arriving stream, and cause the water to flow in a uniform layer over the whole surface of the plane. The ore to be washed is thrown into a trough M (fig. 469), into which a thin stream of water is constantly falling, and where it is constantly kept in motion by a small bucket-wheel, which again is moved by an overshot water-wheel, fed by the canal *oo'*. The ore is thus put in suspension in the water, which, continually flowing into a canal placed lengthwise at the head of the tables, finds its way on to the sleeping-tables through the openings A (fig. 470); and the plane A (fig. 469), on which it first arrives, being too much inclined to allow any ore to deposit, the forming of a deposit first commences on the tables intended for the purpose. Here the richest parts will form the sediment at the higher end of the table, while the poorest grains will only be deposited at the bottom of the inclined plane, or even carried away into the canal *CC'*, which leads them into other canals and depositing reservoirs.

As soon as the table is covered with a sufficient quantity of ore, the workman cuts off the further supply of sludge, and, after having swept all the ore lying between A and *uv* towards A with a broom, allows a current of clear water to flow over the tables, by which the ore is again spread over the latter; and while the poorer parts collect towards the bottom of the inclined plane, that lying on the higher parts can in general be at once sent to the smelting-works.

The table has at *uv* a transverse opening, which remains closed during the washing by a valve, which should not project above the table; but at the close of the operation, the valve being opened, the workman sweeps the sludge through the opening *uv* into boxes placed beneath.

The sleeping-tables are more or less inclined, according to the nature of the ore to be washed; the finest ores requiring the greatest inclination.

§ 744. The percussion-table serves for washing the same kinds of ore as the sleeping-table, the one or the other being preferred according to the nature of the ore and gangue in each special case. The percussion-table consists of an inclined board *BC* (fig. 471), resting on beams of wood to give it greater weight and solidity.

The whole is suspended in the air by four chains or bars of iron  $ab$ ,  $a'b'$ ,  $tt'$ ,  $tt'$ , of which the former two are attached to fixed supports, while the chains  $tt'$ ,  $tt'$  are fixed to a long movable lever  $LL'$ , which turns by the axis  $OO'$ , and serves to vary the degree of inclination of the plank  $BC$ , being held in the height desired by means of iron pins entering the horizontal beam  $xy$ .

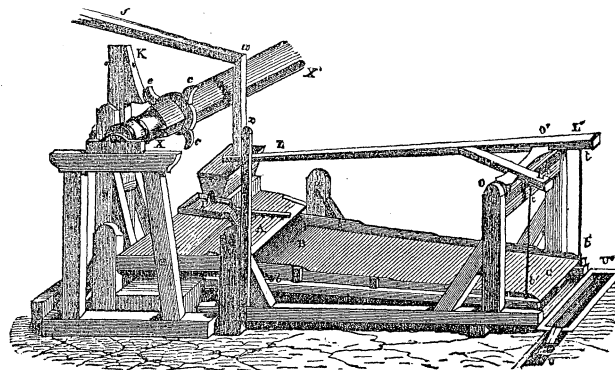


Fig. 471.

The cams  $cc$  on the axle  $XX'$ , which is turned by a water-wheel, act on a curved wooden lever  $K$ , which pushes forward the suspended plank  $BC$ , and immediately abandons it again, so that the latter, falling forcibly back against the wooden supporting beams, receives a violent shock throughout its whole mass. Above the head  $B$  of the suspended plank is a triangular inclined plane  $A$ , fortified with small prisms, and similar to that in fig. 470.

The ore to be washed is heaped in the box  $V$ , which receives a continual stream of water; from there it spreads over the slope  $A$  and the suspended plank  $BC$ , where it has a tendency to deposit. But the violent shocks the plank is constantly receiving, causes the particles to be continually detached and taken into suspension by the water; so that they are then under the most favourable circumstances to be carried off precisely according to the order of their density and size. The inclination of the plank, the violence and frequency of the shocks, and the quantity of water holding the sludge in suspension, are varied according to the nature of the ore to be washed.

§ 745. By these different methods of washing, sludges of greater or less fineness of grain and richness in metal are obtained, and are sorted accordingly. Each of these kinds of sludge is generally subjected to a chemical test, to ascertain their nature and richness in metal. They are then mixed, according to certain proportions which practice has shown to be the most convenient, foreign substances being added if necessary. These mixtures, called *charges*, are then ready for fusion in the furnaces.

The mechanical preparation of ores is one of the most important operations in the extraction of certain metals. Great intelligence is required in the arrangement of such works, as the processes which perfectly succeed in one locality may be quite inefficient in another, where the ore occurs in a different gangue or presents a different state of aggregation.

The adjoined plate gives a connected view of the different apparatus for mechanical preparation and washing just described, as well as the succession of canals and arrangement of the depositing reservoirs, which are generally placed under the flooring of the building. The canals and basins form a large labyrinth, the corresponding parts of which, coming from different washing-machines, unite at points where the muddy water contains similar substances in suspension. The whole apparatus is moved by the same water-wheel RR'.

## MANGANESE.

EQUIVALENT = 28 (350; O = 100.)

§ 746. Manganese\* is obtained by reducing one of its oxides by charcoal at a high temperature. A pure and very dense protoxide, obtained by subjecting carbonate of manganese to strong calcination in a closed crucible, is mixed with  $\frac{1}{10}$  its weight of charcoal and  $\frac{1}{10}$  of fused borax, and heated to the highest possible temperature in a forge-fire, in a "brasqued" or charcoal crucible. The borax added facilitates the union of the metallic globules into a button. The carburetted metal thus obtained is to the pure metal as cast-

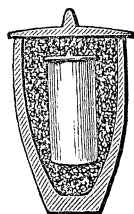


Fig. 472.

iron is to malleable iron, and may be purified by a second fusion with a small quantity of carbonate of manganese, in a small, well-closed porcelain crucible, luted into an earthen crucible, as shown in fig. 472. The manganese thus obtained possesses a certain degree of ductility; and, although it may be filed, breaks under the blow of a hammer, showing a gray fracture much resembling that of certain kinds of cast-iron. Its specific gravity is about 8.0; and it is as difficult of fusion as iron.

Manganese has a great affinity for oxygen, as its surface becomes tarnished by exposure to a moist atmosphere, and covered with dark-brown rust. It decomposes water slowly at ordinary temperatures with the evolution of hydrogen, but effects rapid decomposition at  $212^{\circ}$ . By blowing on a piece of manganese, the same disagreeable odour is perceived which is given off by a carburetted metal dissolving in a weak acid. To preserve the metal, it must be kept from contact with the air, and is therefore generally kept in naphtha, like potassium; but it is better to put the button in a hermetically sealed glass tube.

## COMBINATIONS OF MANGANESE WITH OXYGEN.

§ 747. Five compounds of manganese with oxygen are known; the first of which  $\text{MnO}$  is a strong base; the second,  $\text{Mn}_2\text{O}_3$ , plays the part of a very weak base; the third,  $\text{MnO}_2$ , is neither base nor acid; while the two last,  $\text{MnO}_3$  and  $\text{Mn}_2\text{O}_7$ , are well characterized acids.

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\* Peroxide of manganese has been known for a long time, but it was not until 1774 that Scheele proved it to be a peculiar oxide, from which Gahn obtained the metal several years after.

*Protoxide of Manganese MnO.*

§ 748. Protoxide of manganese is obtained by reducing one of the higher oxides of the metal with hydrogen, or by calcining the carbonate without the contact of air; which is effected by placing

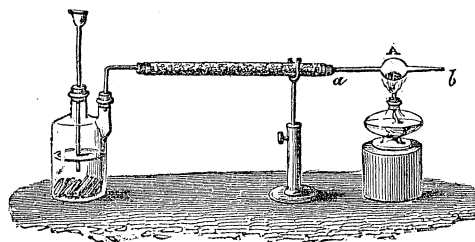


Fig. 473.

the carbonate in a glass bulb A (fig. 473), blown on a tube *ab*, and communicating with an apparatus disengaging dry hydrogen gas. As soon as the air is completely driven out of the apparatus by the hydrogen, the bulb A is heated with an alcohol-lamp;

when the carbonate, disengaging its carbonic acid, leaves the protoxide, the hydrogen preventing the latter from being surrounded by air. The parts *b* and *c* of the tube (fig. 474) are then drawn

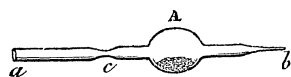


Fig. 474.

out and closed by means of a lamp. The protoxide of manganese thus prepared, is a clear, delicate green powder, which oxidizes rapidly in the air, unless it has been subjected to a slightly elevated

temperature. The protoxide is better aggregated and less changeable when the decomposition of the carbonate has been effected in a porcelain tube strongly heated in a reverberatory furnace.

By heating native peroxide of manganese, or a large mass of carbonate, in a "brasqued" crucible in a forge-fire, a well-aggregated, fine green mass is obtained, which the air does not affect at ordinary temperatures. The surface of the mass often consists of a thin pellicle of reduced metal; but a complete reduction is not propagated by cementation, the immediate contact of charcoal being essential.

Protoxide of manganese is a powerful base. Caustic potassa precipitates it from its solutions as white hydrated protoxide, which rapidly changes into brown sesquioxide by absorbing oxygen from the atmosphere.

*Sesquioxide of Manganese Mn<sub>2</sub>O<sub>3</sub>.*

§ 749. Sesquioxide of manganese Mn<sub>2</sub>O<sub>3</sub> occurs crystallized in nature, both in the anhydrous and hydrated state; the latter much resembling in its external appearance the peroxide, with which it is often associated. But the two oxides are easily distinguished by the colour of their streak or powder, that of the peroxide being dark gray, while that of the sesquioxide is brown.

*Peroxide of Manganese*  $\text{MnO}_2$ .

§ 750. This oxide, the most abundant of all the oxides of manganese, is also the most valuable, from its property of giving with chlorohydric acid the greatest quantity of chlorine. It occurs crystallized in elongated prisms of a gray colour and metallic lustre. Hydrated peroxide of manganese is obtained as a dark-brown powder by decomposing manganate of potassa with hot water, or by passing chlorine through water containing carbonate of manganese in suspension.

By calcining peroxide of manganese in an earthenware retort until the evolution of oxygen ceases, a brown powder containing 27.6 per cent. of oxygen is obtained, with the formula  $\text{Mn}_3\text{O}_4$ . It is generally called *red oxide of manganese*, and, as it behaves as a combination of protoxide with sesquioxide, is often written  $\text{MnO}$ ,  $\text{Mn}_2\text{O}_3$ ; for when it is treated with an acid, protoxide is dissolved and sesquioxide remains.

*Manganic and Permanganic acids*  $\text{MnO}_3$  and  $\text{Mn}_2\text{O}_7$ .

§ 751. The two acid combinations of manganese with oxygen are obtained by treating caustic potassa with peroxide of manganese, either with access of air, or with substances possessing high oxidizing properties. By heating equal proportions of finely powdered peroxide and caustic potassa without access of air, and dissolving the substance obtained in cold water, a green solution is formed, and a mixture of hydrated sesquioxide and binoxide remains as a reddish-brown powder. The green liquid contains, besides some potassa in excess, *manganate of potassa*  $\text{KO}, \text{MnO}_3$ , a portion of the binoxide  $\text{MnO}_2$  having been reduced to sesquioxide  $\text{Mn}_2\text{O}_3$ , by giving off oxygen to another portion of the binoxide, which was thus oxidized to manganic acid  $\text{MnO}_3$ . A greater proportion of manganate of potassa is obtained by making the calcination in the air; or still better, in an atmosphere of oxygen. Some peroxide of manganese, reduced to an impalpable powder, is well mixed with some caustic potassa dissolved in as little water as possible; the paste is dried in a porcelain capsule, and introduced in fragments into a glass tube difficult of fusion, communicating with a retort filled with chlorate of potassa. The tube is heated to a dull-red, and at the same time oxygen is disengaged by heating the chlorate; but, in order to obtain a considerable quantity of manganate, the operation should be continued for some time. The substance gives with cold water an intense emerald-green solution, which, after being filtered through a small plug of asbestos placed in the bottom of a glass funnel, is evaporated under the receiver of an air-pump, over a capsule filled with concentrated sulphuric acid, when beautiful green crystals of manganate of

VOL. II.—C

potassa are obtained, generally mixed with white crystals of hydrated potassa, which may be easily separated by hand. The green crystals are forced from the mother liquid still moistening them, by placing them for a time on a piece of unburned porous clay.

The green crystals of manganate of potassa  $\text{KO}, \text{MnO}_3$  dissolve without change in a solution of caustic potassa, and are again deposited on evaporating the liquid; but on dissolving them in pure water immediate decomposition takes place, the colour of the solution changing to a beautiful red, and a brown precipitate of brown hydrated peroxide being formed. The red solution then contains *permanganate of potassa*  $\text{KO}, \text{Mn}_2\text{O}_7$ . The easy decomposition of manganic acid, even when in combination with as strong a base as potassa, renders it impossible to obtain the acid isolated.

By heating peroxide of manganese with soda or baryta in contact with oxygen, the manganates of soda and baryta are obtained, the latter of which is a green powder, nearly insoluble in water.

When the green mass containing the mixture of manganate of potassa, caustic potassa, and oxide of manganese is dissolved in boiling water, and boiled for several minutes longer, an intense red solution is obtained, which, after being filtered through asbestos and evaporated under the receiver of an air-pump, gives prismatic dark-red crystals of permanganate of potassa. But the most simple process for obtaining this substance in any quantity is the following:—One part of peroxide of manganese, reduced to impalpable powder, is mixed with one part of chlorate of potassa, and one and a quarter parts of caustic potassa, dissolved in the least possible quantity of water, are added: the paste thus formed is dried in a porcelain crucible, during which process a considerable quantity of manganate of potassa already forms. The whole is afterwards heated slowly to a dull-red in an earthen crucible, then boiled with water in a glass flask, filtered through asbestos, and the liquid concentrated in a porcelain capsule over an alcohol-lamp, when, on cooling, crystals of permanganate of potassa are deposited, which may be purified by recrystallization. Permanganate of potassa is not very soluble, as it requires 16 parts of water to dissolve 1 of the salt at  $59^\circ$ , while warm water will dissolve much more.

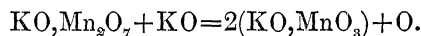
On adding nitrate of silver to a hot solution of permanganate of potassa, fine crystals of permanganate of silver are deposited on cooling, from which other permanganates may be prepared by adding to it an equivalent quantity of a metallic chloride, for the silver combining with the chlorine leaves its permanganic acid to combine with the metal which existed as chloride. After rubbing the two substances with water, the chloride of silver may be separated by decantation or by filtration through asbestos.

Free permanganic acid can be obtained in aqueous solution by decomposing permanganate of baryta with sulphuric acid, added

by drops; when insoluble sulphate of baryta is formed, and the decanted liquid contains permanganic acid. The solution is of a fine red colour, but the acid decomposes easily even in the cold.

Organic substances rapidly decompose the salts of both manganic and permanganic acid by taking up a part of their oxygen, for which reason their solutions must not be filtered through paper. If a red solution of permanganate of potassa, containing caustic potassa, is filtered through paper, the filtrate is generally green from containing manganate; but if the solution is very dilute, or the filtration slow, the liquid completely loses its colour, while the paper takes a deep-brown tinge from the hydrated peroxide which fills its pores.

Caustic potassa, added to a dilute solution of permanganate of potassa, immediately changes the colour of the solution, first to violet and then to a fine emerald-green, the permanganate being reduced to manganate, while another quantity of potassa has entered into combination:



The oxygen remains in solution in the water, since only a small quantity was disengaged, and the permanganic solution is very dilute. The decomposition is owing to the strong basic properties of the potassa, which tends to saturate as much acid as possible. The changing from red to green does not take place instantaneously, and, by adding the potassa in small quantities at a time, the liquid passes through all the intermediate shades between red and green, that is, through all the shades of violet.

It was stated that the colour of a green solution of manganate of potassa changes to red by boiling, hydrated peroxide of manganese being precipitated; but this takes place only when the solution is not too concentrated. Green manganate is also changed to red permanganate in the cold, without any visible precipitation of peroxide, by adding more and more cold water, the oxygen dissolved in which effects the oxidation; the liquid again passing through all the shades produced by a combination of green and red. If it is desirable that the solution should not be very dilute, it is sufficient to leave it in contact with the air, or to pass a current of oxygen through it. The name of *chameleon mineral* has been given to this substance, on account of the phenomena of changing colour.

Manganate of potassa is most rapidly converted into permanganate by the addition of any acid, even of carbonic; but an excess of acid completely discolours the liquid, by forming a salt with the reduced protoxide of manganese, while oxygen is given off.

Of the oxides of manganese, only the protoxide and sesquioxide are bases.



## PROTOSALTS OF MANGANESE.

§ 752. The protosalts of manganese are of an amethyst, or light rose colour, which, however, very soon changes by agitating the liquid in contact with the air, or even by pouring it from one vessel into another.\* Caustic potassa or soda precipitates white hydrated protoxide, which soon changes to brown in the air; while ammonia has the same effect in a smaller degree, a similar phenomena taking place to that mentioned in § 589 for the salts of magnesia, viz. that the ammoniacal salt formed combines with the salt of manganese, and gives a double salt which an excess of ammonia will not decompose. A perfect precipitation cannot therefore be effected, whatever may be the quantity of ammonia added; for, if the salt of manganese is neutral, the first drops of ammonia precipitate some protoxide, but at the same time a corresponding quantity of ammoniacal salt is formed, which is soon present in sufficient quantity to form with the salt of manganese yet in solution a soluble double salt which is not decomposed by ammonia. An excess of ammonia redissolves the hydrated protoxide already precipitated, by entering into combination with it, unless the precipitate has not already changed to brown sesquioxide, which is insoluble in ammonia. By exposing the ammoniacal solution of protoxide to the air, oxygen is absorbed, and the manganese is at last completely precipitated as hydrated sesquioxide.

The alkaline carbonates give a dirty white, and ferrocyanide of potassium a rose-coloured precipitate. The alkaline sulfhydrates precipitate the protosalts of manganese with an orange colour, and sulfhydric acid will not throw them down in the presence of a slight excess of acid, sulphide of manganese being easily decomposed by weak acids.

*Sulphate of Manganese.*

§ 753. Sulphate of manganese is obtained by heating native peroxide with concentrated sulphuric acid, while oxygen is given off; but the residues of red oxide, which remain after the calcination of peroxide for obtaining oxygen gas, are also profitably employed for this purpose. The sulphate is also sometimes prepared by heating the protochloride of manganese obtained by the preparation of chlorine with sulphuric acid. The sulphate crystallizes with different quantities of water, and in different forms, according to the temperature at which the crystallization takes place: thus, when the temperature is below 43°, the crystals contain 7 equiva-

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\* The pink colour of protosalts of manganese I have found to be mostly, if not always, due to the presence of a minute percentage of cobalt, which is rarely absent from the ores of manganese. I have these ores containing from 0.01 up to 7.0 per cent. of oxide of cobalt.—*J. C. B.*

lents of water, and are isomorphous with sulphate of iron,  $\text{FeO}, \text{SO}_3 + 7\text{HO}$ ; while the crystals formed at a temperature between  $43^\circ$  and  $68^\circ$  present the form of sulphate of copper  $\text{CuO}, \text{SO}_3 + 5\text{HO}$ , the sulphate of manganese also containing 5 equivalents of water: lastly, between  $68^\circ$  and  $86^\circ$  the salt crystallizes with 4 equivalents of water, and is isomorphous with the sulphate of iron  $\text{FeO}, \text{SO}_3 + 4\text{HO}$ , which has also been obtained crystallized. These are important facts for the theory of isomorphism.

### *Carbonate of Manganese.*

§ 754. Carbonate of manganese occurs in nature in rhombohedrons, which present the same form as those of carbonate of lime, and are generally of a rose or violet colour. Carbonate of iron and carbonate of lime frequently replace part of the carbonate of manganese in the same crystal, thus offering a new proof of the isomorphism of the protoxides of iron and manganese. Carbonate of manganese may be obtained as a dirty white powder by adding carbonate of soda to a solution of sulphate or chloride of manganese. It is soluble in water containing carbonic acid.

Other salts of manganese are easily obtained by dissolving the carbonate in the corresponding acids.

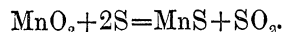
### SESQUISALTS OF MANGANESE.

§ 755. Although sesquioxide of manganese combines with acids, the salts it forms are not durable. By slightly heating hydrated peroxide of manganese with sulphuric acid, the former dissolves with a beautiful red colour, which solution, mixed with sulphate of potassa or ammonia, yields by evaporation octohedral crystals of a true manganic alum  $\text{KO}, \text{SO}_3 + \text{Mn}_2\text{O}_3, 3\text{SO}_3 + 24\text{HO}$ , the existence of which proves sesquioxide of manganese to be a particular oxide, and not a combination of protoxide with peroxide. Oxidizable substances instantly change sesquisulphate of manganese to protosulphate, the liquid losing its colour; a property of the sesquisulphate which is often made use of in the laboratory to ascertain whether an oxide is present in its highest stage of oxidation,—for example, to ascertain whether sulphuric acid contains any sulphurous acid, or whether nitric be free from nitrous acid.

### COMBINATION OF MANGANESE WITH SULPHUR.

§ 756. A hydrated protosulphide of manganese is obtained by adding a solution of an alkaline monosulphide to that of a proto-salt of manganese, when a light-red precipitate is formed, which disengages sulphydric acid on being dissolved in acids. Anhydrous

monosulphide is obtained by heating peroxide of manganese with sulphur, when sulphurous acid is set free :



The excess of sulphur is driven off by heating to redness, but the monosulphide thus prepared is almost always mixed with protoxide, and may be obtained in a state of greater purity by decomposing oxide of manganese with sulphide of carbon at a red-heat.

#### COMBINATIONS OF MANGANESE WITH CHLORINE.

§ 757. Protochloride of manganese is prepared by heating native peroxide with chlorohydric acid, while chlorine is disengaged; but as the native peroxide always contains a certain quantity of iron, the solution usually contains some perchloride of iron, to separate which the solution must be completely evaporated to dryness, by which the excess of chlorohydric acid is also driven off. The residue is dissolved in water, and the liquid boiled for some time with a little carbonate of manganese, which effects the precipitation of the peroxide of iron, while carbonic acid is disengaged, as protoxide of manganese is a much stronger base than peroxide of iron.\*

Protochloride of manganese crystallizes with 4 equivalents of water, one-half of which it gives off at  $212^\circ$ ; but when heated still higher, it becomes completely anhydrous and at last fuses. When fused in contact with the air, the oxygen of the latter expels the chlorine, and the protochloride is converted into protoxide. Experiments have been made to turn this property to technical use, by regaining part of the chlorine contained in the protochloride of manganese, which is a residue in the manufacture of bleaching-powder; and it was effected by roasting the protochloride in reverberatories, and leading the gases, which were highly charged with chlorine, into the chambers where chloride of lime is prepared. The roasting, which was done at as low a temperature as possible, converted the protochloride into sesquioxide, which was treated with chlorohydric acid to obtain a new quantity of chlorine. But, as the oxide thus obtained only gives one-half the quantity of chlorine that an equal weight of peroxide would, and as the operations are too costly, they are no longer continued.

§ 758. Sesquichloride of manganese  $\text{Mn}_2\text{Cl}_3$ , is obtained by treating hydrated sesquioxide with chlorohydric acid, without application of heat. The red solution obtained develops chlorine by heating, and changes into protochloride.

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\* The same insolubility of the perchloride of iron is effected by heating the mixture, when dry, to full redness.—*J. C. B.*

## DETERMINATION OF MANGANESE, AND ITS SEPARATION FROM THE METALS PREVIOUSLY DESCRIBED.

§ 759. The manganese existing in a solution is usually determined by adding carbonate of soda to the boiling liquid, washing the precipitated carbonate of manganese well with boiling water, and calcining it to a high red-heat, by which it is converted into red oxide  $Mn_2O_3$  containing 72.11 per cent. of manganese. The carbonate is dried and calcined with its filter in a platinum crucible, which, being covered with its lid, is placed in an earthen crucible and heated to a strong red-heat. When the liquid from which the oxide of manganese is to be precipitated contains any quantity of ammoniacal salt, it must be evaporated with an excess of carbonate of soda and the residue redissolved in water.

§ 760. Manganese is separated from the alkaline metals by means of carbonate of soda, or by sulphhydrate of ammonia, which precipitates it as sulphide, which, after being washed with water containing some sulphhydrate, is dissolved in an acid, and reprecipitated by carbonate of soda.

It is easily separated from baryta and strontia by adding sulphate of soda to the liquid, which precipitates the baryta and strontia as sulphates. It is separated from lime and magnesia by sulphhydrate of ammonia, which precipitates only the manganese as sulphide, if the solution is sufficiently dilute.

Its separation from alumina and glucina is easily effected by boiling the liquid for some time with an excess of caustic potassa in contact with the air, when the manganese is precipitated as hydrated sesquioxide, while the two earths dissolve in the excess of alkali.

## TESTING THE OXIDES OF MANGANESE.

§ 761. In works where bleaching-powder is made, considerable quantities of peroxide of manganese are used, the commercial value of which depends on the quantity of chlorine it will develop when treated with chlorohydric acid; but, as the native peroxide is always mixed with more or less gangue and sesquioxide of manganese, it is important that the purchaser should be able to determine the quantity of chlorine which a given weight of oxide will develop by a simple process.

One litre of dry chlorine is disengaged by 3.98 gm. of perfectly pure binoxide of manganese at  $32^\circ$  and under the pressure of 760 mm.; and if it be absorbed by a dilute solution of caustic potassa, and water added until the volume of the liquid is 1 litre, a solution is obtained containing precisely its volume of chlorine, and therefore marking 100 chlorometric degrees. But 3.98 gm. of a peroxide of commerce will, when treated in the same manner, give

a solution containing a less volume of chlorine, the quantity of which, when determined by the common chlorometric processes (§ 572), expresses the value of the peroxide employed. Supposing the quantity of chlorine found to be 60, the conclusion follows that the oxide in question only gives a quantity of chlorine represented by 60, while the same weight of pure binoxide yields a quantity represented by 100; and, to obtain the same quantity of chlorine as one kilog. of pure binoxide would give,  $\frac{100}{60} = 1.67$  kilog. of the other oxide must be employed.

§ 762. An average sample of the peroxide to be examined being first made by picking small quantities from all parts of the mass, it is reduced to a fine powder, of which exactly 3.98 gm. are introduced into a small flask A (fig. 475), about 5 centimetres in dia-

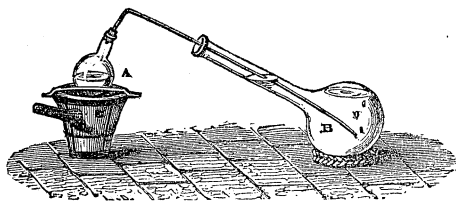


Fig. 475.

meter. By means of a well-fitting cork the flask is furnished with a tube, bent as in the figure, to convey the gas into a long-necked flask B, holding about  $\frac{1}{2}$  litre. The latter is placed in an inclined position, and filled up to the neck with a weak

solution of caustic potassa. The peroxide is introduced into the flask A with a suitable quantity of chlorohydric acid, which is measured in a tube graduated to 25 cubic centimetres; and after adjusting the cork, the temperature is gradually raised. The chlorine first expels the air from the flask A, and causes it to fill the upper part of the bulb B, while the water it displaces rises in the neck. Toward the end of the operation, the liquid in A is heated to the boiling point, so that the steam generated drives all the chlorine into the alkaline liquid. The flask B is then taken away, while the boiling is continued in A to prevent any absorption, and the chlorine is determined in the alkaline liquid by one of the chlorometric methods.

§ 763. A solution of sulphurous acid, perfectly free from sulphuric, may be substituted for the alkaline liquid in the flask B, as the chlorine, when led into the former, converts a corresponding quantity of sulphurous acid into sulphuric, the quantity of which is determined by adding chloride of barium, boiling to expel the excess of sulphurous acid, collecting the precipitate on a filter, and weighing it after calcination. The quality of the peroxide is then proportional to the weight of the sulphate of baryta obtained, 3.98 gm. of pure peroxide giving 10.65 gm. of sulphate of baryta.

As the sulphurous acid used must be perfectly free from sulphuric, it is important to test it to this effect before each determination, which is done by adding a few drops of chloride of barium,

which should give no precipitate. A certain quantity of chloride of barium may at once be added to the liquid, so that sulphate of baryta forms as the sulphurous acid oxidizes by the oxygen of the air; and when the solution is to be used, the clear liquid, which of course is free from sulphuric acid, can be decanted off from the precipitate.

The best method of conducting the experiment is that represented in fig. 476. Water, freed from air by boiling, and some

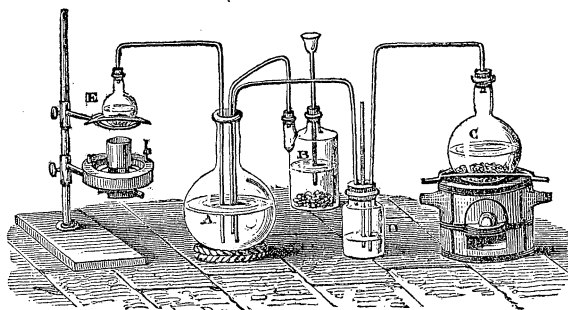


Fig. 476.

chloride of barium, are introduced into the flask A, into which, as soon as the water has cooled, a current of hydrogen is led, supplied by the generator B. As soon as the air is expelled from A by the hydrogen, a current of sulphurous acid gas is introduced, obtained by heating concentrated sulphuric acid with copper or mercury in the flask C, and purifying it by washing with water in the small flask D. Lastly, the 3.98 gm. of peroxide are heated in the flask E with chlorohydric acid, and the chlorine disengaged is led into the flask A, where it oxidizes a corresponding quantity of sulphurous acid to sulphuric, which precipitates as sulphate of baryta, while there is no fear that sulphuric acid might form by the contact of sulphurous with the air. Toward the end of the operation the liquid in A is boiled to expel the excess of sulphurous acid, the oxidation of which is still prevented by continuing the stream of hydrogen; and finally the sulphate of baryta formed is collected on a filter.

§ 764. The finely powdered oxide of manganese may also be heated with a concentrated solution of oxalic acid, which forms protoxalate of manganese, while the oxygen given off by the reduction of the higher oxides to protoxide converts a corresponding quantity of oxalic into carbonic acid, which may be precipitated as carbonate of baryta by being led into a solution of baryta, or better still, may be conducted into a weighed bulb-apparatus containing a concentrated solution of caustic potassa, the increase of weight of which after the operation corresponds exactly to the carbonic

acid. In either case the gas must be dried by being passed through a tube containing concentrated sulphuric acid.

§ 765. For an accurate estimation of the value of an oxide of manganese it is not sufficient merely to determine the quantity of chlorine it will develop, but the quantity of chlorohydric acid required to disengage the chlorine must also be found. If the oxide is pure binoxide, the chlorine of one-half of the acid is necessarily disengaged, while pure sesquioxide will only give one-third of the chlorine; for which reason, in the latter case, one and a half times the quantity of acid is required to give the same quantity of chlorine as when pure binoxide is used; and lastly, if the oxide is mixed with a gangue of lime, baryta, or oxide of iron, these bases will neutralize a part of the acid without disengaging chlorine. To find the quantity of chlorine required, the acidimetric percentage of 25 cubic centimetres of the acid employed is first determined, and 3.98 gm. of the oxide of manganese are treated with other 25 cubic centimetres of the same acid, the flask containing the mixture being kept heated. The chlorine is lost, but the small quantity of chlorohydric acid which might distil over is condensed in a moist flask through which the gas is led. When all the chlorine is disengaged, the small quantity of liquid in the moist flask is added to the residue in the flask in which the gas was developed, the liquid is diluted to the volume of half a litre, and the remaining acid is determined by adding a standard alkaline solution until the precipitate of hydrated oxides, which forms on the addition of every drop, is no longer redissolved by shaking the liquid. This experiment gives the quantity of acid which has remained free, and shows, when compared with the former experiment, the quantity of acid required by the oxide of manganese.\*

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\* The following is a shorter method of testing peroxides of manganese. The chlorine disengaged from a weighed quantity of the oxide is conducted into the solution of a given quantity of a protosalt of iron, an equivalent quantity of which it oxidizes to peroxide; so that, if the remaining quantity of protoxide of iron which is determined with permanganate of potassa (as will be described in § 804) be subtracted from the quantity contained in the protosalt employed, the difference will be in proportion to the chlorine disengaged.

The protosalt of iron best adapted to the purpose is the protosulphate of iron and ammonia, which is easily obtained by mixing equal volumes of saturated solutions of sulphate of iron and sulphate of ammonia, when the liquid on evaporating yields prismatic crystals of the salt, the formula of which is  $\text{FeO}, \text{SO}_3 + \text{NH}_4\text{O}, \text{SO}_3 + 6\text{HO}$ . One hundred grammes of the salt are dissolved in 1837 cubic centimetres of water, so that the solution contains 5.44 per cent. of the salt; or, 544 parts of the salt corresponding to 184 parts of pure protoxide, exactly one per cent. of protoxide of iron: and the standard solution thus obtained, which is best prepared in larger quantities at a time, is used for all chlorometric determinations, as well as for that of chrome.

Supposing the quantity of oxide subjected to the test to be exactly one gramme, and the substance to be pure peroxide, which gives one equivalent of chlorine; then will the quantity of chlorine developed be 0.807 gm.; and supposing the quantity of the standard solution of iron employed to be 200 cubic centimetres, which contain 2 gm. of protoxide, only 1.63 of which are oxidized by the chlorine;

then will the 0.37 gm. of protoxide, determined directly by permanganate of potassa, and subtracted from the 2 gm. employed, give the quantity of protoxide which was oxidized, viz. 1.63 gm., which correspond to 0.807 gm. of chlorine, as one equivalent of chlorine oxidizes two equivalents of protoxide of iron.—*W. L. F.*

Another method of determining the commercial value of peroxide of manganese, better than that described in the text, is to employ dry oxalate of soda, which is easily prepared and preserved, and of which  $152\frac{1}{4}$  grains are just sufficient for 100 grs. of pure binoxide, in order that its oxalic acid may be wholly converted into 100 grs. of carbonic acid. 76 grs. of the dry oxalate and 50 grs. of the peroxide are introduced with about  $\frac{1}{2}$  oz. of water into a small flask containing two tubulures, through one of which an S-tube passes, and through the other a small tube connected with a tube of sulphuric-pumice or chloride of calcium. The whole apparatus being weighed at once, together with about 200 grs. of oil of vitriol, the latter is gradually poured through the S-tube into the little flask. The oil of vitriol disengages the oxalic acid, which is oxidized into carbonic acid by the excess of oxygen over that in the protoxide, and since it cannot pass through either escape-tubes without being dried, the loss of weight of the whole apparatus indicates the loss of carbonic acid alone. The number of grains of loss being doubled, gives the percentage of peroxide equivalent to pure binoxide. The different methods of arranging the apparatus will be found in the analytical chemistries of Rose and Fresenius, and others, and in the *Encyclop. of Chem.* The best commercial varieties contain from 80 to 98 per cent. of binoxide.—*J. C. B.*



## IRON.

EQUIVALENT = 28.0 (O=100; 350.0).

§ 766. On account of its numerous technical applications, iron is the most important of all the metals. It is used in three states :

1. *Bar* or malleable iron.
2. Steel.
3. *Crude* or cast-iron.

Steel and cast-iron are combinations of iron with small but variable quantities of carbon and silicium.

The bar-iron of commerce is not chemically pure, as it contains a small quantity of carbon, and often traces of silicium, sulphur, or phosphorus, which latter remarkably affects its quality. The iron used in fine locksmith's work approaches a state of purity; but the purest iron is found in piano-forte wires, or ordinary wire, because only iron of great purity can be drawn out into very fine threads.

In order to obtain iron chemically pure, some wire is cut into pieces of the same length, and tied in bundles; when their surface is oxidized, by heating them for a few moments exposed to the air, or better still, in a porcelain tube through which steam is passed. The bundles of oxidized iron are then placed in a small porcelain crucible with a small quantity of powdered glass; and the crucible being set in a second earthen crucible, luted externally with clay, is heated in a blast-furnace at the highest temperature that can be produced. The small quantities of foreign matter contained in the iron, are burned by the oxygen of the oxide, while the excess of oxide of iron, combining with the glass, forms a slag. If the temperature be sufficiently elevated the purified iron fuses to a single lump. Pure iron is whiter and more malleable than the iron of commerce, but less tenacious.

Pure iron may likewise be obtained by the reduction of one of its oxides by hydrogen, which takes place at a dull red-heat, and may be effected in the small apparatus described (fig. 473) for the preparation of the protoxide of manganese. The metallic iron remains in the tube, in the form of a grayish-black powder, which may be preserved by closing hermetically both ends of the tube while it is filled with hydrogen gas; for very finely divided iron has so great an affinity to oxygen that it is inflamed by contact with the air; a property which has given to it the name of *pyrophoric iron*. If the reduction be made in a porcelain tube at a high temperature, the metal becomes solid, assuming a metallic lustre, and no longer oxidizing in dry air.

Perfectly pure iron may also be procured, by heating protochloride of iron in a glass tube, through which a current of hydrogen gas is passed; when the iron forms on the sides of the glass a glittering, brilliant coating, in which small cubic crystals may often be seen.

§ 767. The texture of commercial iron varies greatly, according to its mode of manufacture. Pure iron which has been forged and rolled equally in all directions, exhibits a texture of very small, brilliant grains; but, when drawn out into bars, its texture is often decidedly fibrous, the fibres always running in the direction of the bar, which may be readily proved by breaking the latter. The fibrous texture is highly esteemed, because the iron possessing it is much more tenacious than granular iron, and bears a greater weight without breaking. The fibrous texture of iron is generally regarded as an index of its good quality; however, skilful workmen can impart this quality also to bars of an inferior sort. Iron of fibrous texture does not always remain in that state, but after some time changes into the granular, or even the laminated texture; which change ensues most rapidly when the bars are subjected to vibration, as, for instance, when they support the floor of a suspension-bridge. The tenacity of the metal diminishes at the same time in a remarkable manner, and it frequently breaks with a load which the bar would easily have borne when its texture was fibrous. A change of this kind is frequently observed in the axles of locomotives and railway-cars.\*

The specific gravity of wrought-iron varies from 7.7 to 7.9. Iron is the most tenacious of all the metals, a cylindrical iron-wire of 2 millimetres in diameter being able to sustain a load of 250 kilogs.

§ 768. The highest temperature that can be produced in a blast-furnace is required for the fusion of iron, which, however, is more easy when it can be combined with carbon. Iron passes from the fluid to the solid, through the doughy state, and therefore belongs to that class of substances which crystallize with difficulty by fusion. However, if large masses of iron, heated to a very high temperature, be allowed to cool very slowly, indications of crystallization of the cubic form are found in the interior of these masses.† Heated to a white-heat, iron becomes sufficiently soft to assume any form under the hammer; and two bars, when heated to redness, can be readily soldered to each other without the interposition of another metal, when the surfaces to be joined are completely free from oxide.

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\* The fibrous texture of iron is also changed to the granular by heating the metal to redness, and immersing it while hot into cold water.—*W. L. F.*

† Some species of cast-iron, as, for example, that made from the manganiferous sparry iron-ore of Muesen in Westphalia, and that made at Easton, in Pennsylvania, the latter of which is remarkable for its extreme ductility when converted into bar-iron, show a laminated texture, which is owing to its being an aggregated mass of laminated prismatic crystals, the angles of which are about  $112^\circ$ .—*W. L. F.*

VOL. II.—D

Now, as it is known that iron heated in the air soon oxidizes, the blacksmith generally throws a small quantity of sand upon the bars he wishes to solder, which, by combining with the oxide of iron, produces a very fusible silicate, which, forming a kind of varnish on the surface of the metal and preventing its further oxidation, is afterward, from its extreme fluidity, entirely driven off by the blows of the hammer.

§ 769. Iron, cobalt, and nickel are the only metals which are remarkably magnetic at the ordinary temperature. A piece of pure iron immediately becomes a magnet, either by contact with or at a short distance from a native magnet, its magnetic properties disappearing again as soon as the magnet is removed; but if the iron is combined with a small quantity of carbon, if it is *steely*, the magnetism is slower of development, but continues longer after the removal of the magnet. A bar of steel, rubbed against a magnet, acquires permanent magnetic properties, and becomes a true magnet. The magnetic properties of iron diminish rapidly with the temperature, an iron ball heated to a whitish red-heat no longer exerting any influence over the needle, but recovering its magnetic virtue on cooling.

§ 770. Iron remains unchanged for an indefinite time in dry air, and even in dry oxygen, at the ordinary temperature; but soon alters in moist air, by becoming covered with *rust*. The rust of iron, which consists of an oxidation of its surface, is most readily formed in the presence of carbonic acid, of which the air always contains a small quantity. Under the influence of the carbonic acid and the oxygen, the surface of the iron is converted into proto-carbonate, which, on absorbing a new portion of oxygen, is transformed into hydrated peroxide of iron, while the carbonic acid disengaged favours the oxidation of an additional quantity of metallic iron. It has been observed, that when iron has begun to rust at any particular point, it changes very rapidly around this point, which is produced by a galvanic phenomenon accelerating the oxidation. The iron and thin layer of oxide which forms on its surface constitute the two elements of a pile in which the iron becomes positive, and thus acquires an affinity for oxygen sufficiently great to decompose water at the ordinary temperature, with the evolution of hydrogen gas. This phenomenon is rendered very evident by allowing moist iron-filings to rust in the air, when, after some time, the odour exhaled by hydrogen gas\* made from the carburetted metals is easily recognised. Rust almost always contains a small quantity of ammonia, the presence of which may be recognised by heating it with potassa, and is explained as follows:—It has been shown (§ 122)

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\* This peculiar odour is not exhaled by hydrogen gas, but is that of a certain substance called *ozone*, and shown by Bunsen to be a combination of one atom of hydrogen with three of oxygen, which forms under almost all circumstances where a galvanic current is active.—*W. L. F.*

that when hydrogen and nitrogen meet in the nascent state in a liquid, they combine and form ammonia: now, the water which moistens the rust, being in contact with the air, contains nitrogen in solution, and on the other hand, hydrogen is disengaged by the decomposition of the water. The circumstances under which ammonia can form by the direct combination of hydrogen and nitrogen are therefore realized. The peroxide of iron, which acts with very powerful bases the part of a feeble acid, retains the ammonia and prevents it from being disengaged.

It is important to be aware of the presence of ammonia in rust, as it has been long since admitted, that when spots of rust which were found on sidearms or steel weapons, suspected to have been used in the commission of a crime, evolved ammonia by contact with potassa, it was a proof that the rust was formed by contact with animal matter, and these spots of blood were the cause of its presence. This presumption was erroneous; for as we have just seen, steel-rust formed by the contact of air alone may contain an appreciable quantity of ammonia.

Rust soon changes in fresh water, but very slightly in water containing a few thousandths of carbonate of soda or potassa. During the last few years, iron has been preserved from rust by covering its surface with a very thin layer of metallic zinc,\* and iron thus coated is called *galvanized iron*. This phenomenon was explained in § 305.

Iron soon oxidizes by contact with the air when heated to redness, becoming covered with a black pellicle of oxide, which falls off under the hammer. To this easy combustion of iron in the air may be attributed the property which it possesses of giving out sparks when struck by a flint, in which case small particles are detached, which, being strongly heated by friction against the flint, become incandescent by combining with the oxygen of the air, and may easily inflame combustible substances, such as tinder. If the steel be struck for some time over a sheet of white paper, the latter will be covered with small black particles, which are attracted by the magnet, and are, in fact, small spherical globules of magnetic iron.

§ 771. Iron is readily acted on by chlorohydric acid, protochloride of iron being formed, and hydrogen disengaged. Dilute cold sulphuric acid dissolves it with the evolution of hydrogen, while the concentrated acid also attacks it, but disengages sulphurous acid. Concentrated nitric acid attacks it sharply with a copious

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\* A patent has lately been taken out in Europe (Vienna?) for preserving iron from rust by a coating of metallic cadmium, which at the same time imparts a silvery lustre to the surface. Silicate of potassa, the German *wasserglas*, has also been employed.—W. L. F.

disengagement with nitrous fumes,\* while the dilute acid dissolves it without any apparent evolution of gas, forming at the same time protonitrate of iron and nitrate of ammonia (122).

#### COMPOUNDS OF IRON WITH OXYGEN.

§ 772. Three compounds of iron with oxygen are known :

1. A protoxide  $\text{FeO}$ , which is a powerful base, isomorphous with the bases of which the formula is  $\text{RO}$ .

2. A sesquioxide  $\text{Fe}_2\text{O}_3$ , being a very feeble base, analogous to alumina, and isomorphous with the oxides of which the formula is  $\text{R}_2\text{O}_3$ .

3. Lastly, an acid  $\text{FeO}_3$ , analogous to manganic acid.

A fourth compound of iron with oxygen, of the formula  $\text{Fe}_3\text{O}_4$ , is also known, and is called *magnetic oxide*; but as it behaves like a compound of protoxide and sesquioxide  $\text{FeO}, \text{Fe}_2\text{O}_3$ , it is regarded as such.

#### *Protoxide of Iron $\text{FeO}$ .*

§ 773. Protoxide of iron has hitherto not been obtained in a state of purity. When a large bar of iron heated to redness is allowed to cool slowly in the air, its surface oxidizes, and a black pellicle of a metallic lustre is formed, which falls off under the hammer, and is called *finery cinder*. If a thin piece of cinder be examined with a lens, it is seen to be composed of several layers; the outer stratum showing nearly the composition of magnetic oxide  $\text{Fe}_3\text{O}_4$ , while the inside layer, or that immediately in contact with the metal, resembles the protoxide very closely.

If a solution of caustic potassa be added to a protosalt of iron, a white precipitate of *hydrated protoxide* is obtained, which soon turns green on exposure to the air, by forming hydrated sesquioxide by absorption of oxygen. If boiling solutions be used, and the ebullition prolonged for some time, the white precipitate loses its water of hydration and becomes black; but the oxide has such an affinity for oxygen that it is impossible to collect it unchanged. It even decomposes water at the boiling point, and is ultimately converted into magnetic oxide.

French bottle-glass owes its hue to the presence of this oxide (§ 684), which imparts a deep green colour to fluxes.

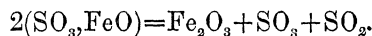
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\* Very concentrated nitric acid will not dissolve pure iron at all, owing to an electrical phenomenon by which the iron is brought to the *passive state*, and changes its electropositive power. The iron will continue in this state, and not be attacked by the acid, even on diluting the latter to almost any degree; but on touching the piece of passive iron, lying in the diluted acid, with a piece of common iron, such as a key, the galvanic current produced by the contact of the two pieces, whose electromotive power is yet different, instantly changes the passive iron back to its natural state, and renders it soluble.—*W. L. F.*

*Sesquioxide of Iron*  $\text{Fe}_2\text{O}_3$ .

§ 774. The sesquioxide  $\text{Fe}_2\text{O}_3$ , or peroxide, is a substance abundantly met with in nature, occurring either in the anhydrous or the hydrated state. The anhydrous peroxide forms flattened rhombohedral crystals, very brilliant and nearly black, while their powder is of a deep red colour. Mineralogists call it *specular iron*: it is found in veins in the old rocks. In the fissures of volcanic lavas, thin and brilliant laminæ of peroxide of iron are often found, having the form of regular hexagons, and also belonging to the class of specular iron. Anhydrous peroxide of iron, which is also found in compact masses, of an intense red colour, is called by mineralogists *red hematite*, and is known in the arts by the name of *bloodstone*, a substance extensively employed for polishing metals.

Peroxide of iron is prepared artificially by calcining protosulphate of iron, when sulphurous and sulphuric acids are disengaged, and the peroxide remains in the form of a red powder:



Peroxide of iron thus prepared is known by the name of *colcothar*, and used for painting, for polishing silver, and for giving the last polish to mirrors. The intensity of colour of peroxide of iron is in proportion to its compactness.

Peroxide of iron may be obtained in the form of small crystalline lamellæ, of great lustre and nearly black, by calcining in a crucible 1 part of sulphate of iron with 3 parts of sea-salt. The calcined matter is treated with boiling water, which leaves the peroxide.

§ 775. *Hydrated peroxide of iron* is prepared by adding potassa or ammonia to the solution of a sesquisalt of iron, when a copious brown precipitate is formed. When the reaction has been effected by caustic potassa, the precipitate always retains a small quantity of alkali, which is removed with difficulty only by prolonged boiling with pure water. The precipitation may be made by a solution of carbonate of potassa or soda, in which case the precipitate is also hydrated peroxide of iron, the carbonic acid being disengaged, or combining with the excess of neutral carbonate, which it transforms into bicarbonate.

Hydrated peroxide of iron parts readily with its water by the application of heat, but when heated still further, a temperature is soon attained at which the oxide suddenly becomes incandescent from a spontaneous evolution of heat. This incandescence is only momentary, and the temperature of the oxide again falls to that of the vessel in which it is heated; but its physical and chemical properties have been remarkably modified, as it has become more compact, and dissolves with great difficulty even in highly concen-

trated acids. Sesquioxide of iron, heated to a high white-heat, loses a portion of its oxygen, and is converted into magnetic oxide  $\text{Fe}_3\text{O}_4$ .

Peroxide of iron colours fluxes of a reddish yellow, but a considerable quantity is necessary to produce this effect in glass. The small quantity of protoxide which imparts a deep green hue to a vitreous flux, does not colour it appreciably when converted into peroxide (§ 674).

*Magnetic oxide of iron  $\text{Fe}_3\text{O}_4$ .*

§ 776. A native oxide of iron, intermediate between the protoxide and peroxide, is often found in very regular, brilliant octahedrons, of a fine metallic lustre. At other times it is found in the old rocks in compact masses, often very large, and is worked as an iron ore. Large quantities of it are found at Dannemora, in Sweden, and from this ore the best quality of iron is obtained. This compound has been called *magnetic oxide*, from its possessing very highly developed magnetic properties. Native loadstone is formed of this oxide of iron.

Magnetic oxide of iron is only produced when iron burns at a high temperature in the air, or in oxygen; for example, by the rapid combustion of iron-wire in pure oxygen (§ 64). But the most certain method of obtaining it in the laboratory consists in heating iron-wire in a porcelain tube, in a current of steam, as in the experiment described in § 68, when the surface of the wire becomes covered with an infinite number of small, very brilliant crystals, which by the aid of a lens are seen to be regular octahedrons, resembling those of the native magnetic oxide.

This oxide may also be obtained in the hydrated state, by dissolving the magnetic oxide in chlorohydric acid, and adding a large excess of ammonia, when a deep green precipitate, becoming black by desiccation, is formed. This hydrate is magnetic, like the anhydrous oxide. Hydrated magnetic oxide may likewise be prepared by pouring into ammonia a mixture of equal equivalents of persulphate and protosulphate of iron. In order to make this mixture, two equal volumes of the same solution of protosulphate of iron are used, one of which is transformed into persulphate by evaporating it to dryness with nitric and sulphuric acids, and then redissolved in the other volume of protosulphate.

The magnetic oxide does not behave like an oxide *per se*, but rather like a compound of protoxide and peroxide. Its formula is properly  $\text{FeO}, \text{Fe}_2\text{O}_3$ , analogous to that of red oxide of manganese  $\text{MnO}, \text{Mn}_2\text{O}_3$ . The solution of magnetic oxide in an acid possesses the properties of a mixture of a protosalt with a sesquisalt; and if an alkali is dropped into the liquid, the peroxide is precipitated before the protoxide. In order to precipitate the two oxides in

combination the proceeding must be inverted, and the solution of the salt of iron be poured into the alkaline liquid. We shall, moreover, soon see several compounds presenting a similar chemical formula, and affecting identical crystalline forms, but in which the peroxide of iron is often replaced by alumina or by oxide of chrome, while magnesia, protoxide of manganese, or oxide of zinc often take the place of the protoxide.

*Ferric acid*  $\text{FeO}_3$ .

§ 777. The third compound of iron with oxygen possesses the properties of an acid corresponding with manganic acid, and is formed under the same circumstances. A mixture of iron filings and nitrate of potassa is heated to redness in an iron crucible, when a beautiful red solution of ferrate of potassa is obtained by treating the mass with water, resembling permanganate of potassa in colour. It is also procured by passing chlorine through a concentrated solution of caustic potassa, containing hydrated peroxide of iron in suspension. Pieces of caustic potassa are added from time to time, in order constantly to maintain a large excess of alkali in the liquid. Ferrate of potassa, being nearly insoluble in a concentrated solution of potassa, is deposited in the form of a black powder, which may be almost entirely separated from the mother liquid by drying it on unglazed porcelain. Ferrate of potassa is still less fixed than the manganate, and has not yet been obtained in a crystalline form. Its solution cannot be filtered through paper, as it immediately decomposes when in contact with organic matter, forming hydrated sesquioxide of iron.

§ 778. The following is the composition of the four oxides of iron :

Protoxide $\text{FeO}$ .....	Iron .....	77.78 .....	28
	Oxygen.....	22.22 .....	8
		<hr/> 100.00 .....	<hr/> 36
Sesquioxide $\text{Fe}_2\text{O}_3$ .....	Iron .....	70.00 .....	56
	Oxygen.....	30.00 .....	24
		<hr/> 100.00 .....	<hr/> 80
Magnetic oxide $\text{FeO}, \text{Fe}_2\text{O}_3$ .....	Iron.....	72.42 .....	84
	Oxygen.....	27.58 .....	32
		<hr/> 100.00 .....	<hr/> 116
Ferric acid $\text{FeO}_3$ .....	Iron.....	53.84 .....	28
	Oxygen.....	46.16 .....	24
		<hr/> 100.00 .....	<hr/> 52

The equivalent of iron is 28, or 350 when that of oxygen is assumed as 100.



## SALTS OF PROTOXIDE OF IRON.

§ 779. The hydrated protosalts of iron are of a bright green colour, which they nearly lose by parting with their water; and their solutions are also of a bright green. Their taste is astringent and metallic.

Potassa and soda, poured into the solution of a protosalt of iron, yield a white precipitate, which immediately turns green by contact with the air, and, when left exposed to the atmosphere for an indefinite time, becomes ochrous, and is converted into hydrated sesquioxide. This property distinguishes the protosalts of iron from those of manganese, the latter yielding with the alkalies a white precipitate, which turns brown in the air, without passing through the intermediate green.

Ammonia produces with the protosalts of iron a reaction resembling that with the salts of manganese (§ 752). An excess of ammonia redissolves the protoxide; but by absorbing the oxygen of the air, the liquid soon becomes clouded, and hydrated sesquioxide is precipitated.

The alkaline carbonates, poured into a very cold solution of a protosalt of iron, throw down a white precipitate of protocarbonate, which, not being very fixed, soon parts with its carbonic acid.

Sulphydric acid does not precipitate the protosalts of iron, however slightly acid they may be, while the sulphydrates give black precipitates.

Yellow ferro-cyanide of potassium yields a white precipitate, which soon turns blue by absorbing the oxygen of the air.

The red ferro-cyanide gives a beautiful deep-blue precipitate.

Succinate and benzoate of ammonia do not precipitate the protosalts of iron.

Phosphate of potassa gives a white precipitate, which turns blue by exposure to the atmosphere.

Arseniate of potassa yields a white precipitate, which turns green in the air.

Tannin forms no precipitate with the protosalts of iron, but the liquid soon blackens in the air.

*Protosulphate of Iron.*

§ 780. The sulphate is the most important of the protosalts of iron, being used in dyeing, under the name of *green vitriol*, or *copperas*. It is prepared in the laboratory by dissolving metallic iron in dilute sulphuric acid, when hydrogen is disengaged. This process is sometimes adopted in the arts; but copperas is generally obtained from the native sulphides of iron or *pyrites*, which are abundantly found in nature, but cannot be used as iron

ores, because the reduction of the metal would be too expensive, and iron of an inferior quality would be obtained; but as the pyrites frequently contain some hundredths of sulphide of copper, this metal is extracted from them. For this purpose they are roasted, by a process hereafter to be described, when the metals are oxidized, and a great portion of the sulphur is disengaged in the state of sulphurous acid, while another portion is oxidized still higher, and, by combining with the metallic oxides as sulphuric acid, yields sulphates which are removed by washing.

In some localities sulphur is obtained from pyrites by calcining them in retorts, when a portion of the sulphur is disengaged, and a disaggregated magnetic sulphide of iron remains in the retort, absorbing rapidly the oxygen of the moist air, and changing into a sulphate.

In other localities, schistous rocks filled with small crystals of pyrites are found, which sometimes change rapidly in the air and *fall*; that is to say, soon become reduced to powder. The sulphide of iron is then changed into a sulphate, while the schist itself is more or less decomposed, and yields sulphate of alumina, when the two sulphates are dissolved in water.

The vitriolic liquids are evaporated in leaden boilers, and conducted, when suitably concentrated, into a large vat, where they are allowed to settle for some time, and then are run off into large crystallizing-vats. Strings, on which the crystals of sulphate of iron form, are suspended in the liquid. When the mother liquid yields no more crystals of the sulphate, even after additional concentration, it is used for the preparation of alum. The water contains sulphate of alumina, which crystallizes with difficulty; but an addition of sulphate of potassa soon effects the deposition of crystals of alum, which are purified by recrystallization.

The sulphate of iron of commerce is often covered with a basic persulphate, rendering its surface ochreous, which is removed by dissolving it in water and boiling the solution with iron filings, which reduce the sesquisulphate of iron to protosulphate. Sulphate of iron crystallizes at the ordinary temperature with 7 equivalents of water, while the crystals deposited at  $176^{\circ}$  contain only 4 equivalents. The same salt readily parts with a portion of its water when heated, but a temperature of nearly  $572^{\circ}$  is requisite to drive off the last particles of it. Dishydrated sulphate of iron forms a white powder, which, if heated still further, is decomposed by disengaging sulphurous and sulphuric acids, while peroxide of iron remains (§ 138). 100 parts of water at  $59^{\circ}$  dissolve 73 of crystallized sulphate, and at  $212^{\circ}$  more than 300 parts.

#### *Protonitrate of Iron.*

§ 781. This salt is obtained by dissolving metallic iron in cold dilute nitric acid, when a certain quantity of nitrate of ammonia

is also formed, which combining with the nitrate of iron, produces a double salt, which is deposited in crystals. The formation of nitrate of ammonia is owing to the fact, that while the iron is being oxidized at the same time at the expense of the oxygen of the water and of that of the nitric acid, hydrogen and nitrogen gas are simultaneously disengaged, and combine in the nascent state to form ammonia. The best method of obtaining protonitrate of iron consists in decomposing a solution of protosulphate of iron by nitrate of baryta.

#### *Carbonate of Iron.*

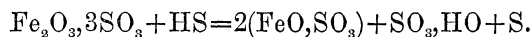
§ 782. Carbonate of iron is found in nature as *sparry iron*, crystallized in rhombohedrons, resembling those of carbonate of lime, and is highly esteemed as an ore. It is found in veins in the old rocks. Carbonate of iron, heated in an earthen retort, yields magnetic oxide of iron as a residue, and disengages a mixture of carbonic oxide and acid.

Carbonate of iron has not yet been artificially prepared.

#### *Sesquisalts of Iron.*

§ 783. These salts are prepared by dissolving the hydrated peroxide in acids, or by subjecting the protosalts to an oxidizing agency in the presence of an excess of acid. Thus, protosulphate of iron is converted into a persulphate by heating it with nitric acid, while reddish vapours are given off, and the substance becomes brown. This colour is owing to the fact that the deutoxide of nitrogen which is formed dissolves in the undecomposed protosulphate, and produces a highly coloured liquid (§ 114). But protosulphate of iron  $\text{FeO}, \text{SO}_3$  can only be converted into neutral persulphate  $\text{Fe}_2\text{O}_3, 3\text{SO}_3$  by adding a certain quantity of sulphuric acid. The salts of protoxide of iron are likewise changed into salts of peroxide by treating their solution with chlorine, in the presence of an excess of acid.

Reciprocally, it is easy to transform a sesquisalt of iron into a protosalt, by subjecting it to a deoxidizing action: for example, by boiling its solution with iron filings, or treating it with sulphuric acid, in which latter case sulphur is deposited, rendering the liquid milky:



§ 784. The salts of peroxide of iron afford yellow precipitates, the colour of which is deeper in proportion as they approach neutrality.

The fixed alkalis and ammonia yield a brown precipitate of hydrated peroxide, insoluble in an excess of ammonia.

The alkaline carbonates give the same brown precipitate of hydrated peroxide.

Sulphydric acid produces a white precipitate of very finely divided sulphur (§ 783), while the sulphydrates give brown precipitates.

Yellow prussiate of potash gives a beautiful blue precipitate.

Red prussiate does not precipitate the sesquisalts of iron. These two characters signally distinguish the salts of peroxide of iron from those of protoxide.

Benzoate and succinate of ammonia give brown precipitates.

The sesquisalts of iron rarely exist in the neutral state, as their solutions always contain an excess of acid. A neutral salt is decomposed by treatment with water into a very basic salt which is precipitated, and an acid salt which remains in solution.

Persulphate of iron forms alum with the sulphates of potassa and ammonia, the formulæ of which correspond to those of ordinary alum, namely,  $\text{Fe}_2\text{O}_3, 3\text{SO}_3 + \text{KO}, \text{SO}_3 + 24\text{HO}$  and  $\text{Fe}_2\text{O}_3, \text{SO}_3 + \text{NH}_4\text{O}, \text{SO}_3 + 24\text{HO}$ . They crystallize in regular octahedrons of a violet hue, and are obtained by adding sulphate of potassa or of ammonia to a solution of persulphate of iron, prepared by the process indicated (§ 776,) and evaporating the liquid at a low temperature. These alums are easily destroyed by heat.

#### COMPOUNDS OF IRON WITH SULPHUR.

§ 785. Several compounds of iron with sulphate are known.

##### *Protosulphide of Iron* $\text{FeS}$ .

§ 786. Protosulphide of iron is obtained by direct combination of iron with sulphur. When an iron bar, heated to whiteness, is plunged into fused sulphur, the combination takes place with great evolution of heat, the bar becomes corroded, and the fused sulphide of iron falls to the bottom of the crucible. A more convenient method of preparing it consists simply in heating a mixture of iron filings and sulphur in a crucible. Protosulphide of iron combines readily with an excess of iron, producing sub-sulphides, which are met with in several metallurgic processes; and it also combines very easily with a greater proportion of sulphur. In order to obtain pure protosulphide of iron, the product formed in the presence of an excess of sulphur must be fused in a crucible covered with damp charcoal, in a forge-fire; when the excess of sulphur is disengaged in the state of sulphide of carbon, and protosulphide remains in the form of a lump possessing a metallic lustre.

This sulphide is obtained hydrated in the form of a black powder, when a protosalt of iron is precipitated by a solution of an alkaline sulphydrate.

Sulphur and iron combine together in the presence of water, even at the ordinary temperature. If iron filings and flowers of sulphur are intimate mixed in an earthen vessel and moistened with water, the temperature soon rises, while the colour of the

paste becomes deeper, and, in a few hours, the two substances have combined together. This preparation is sometimes made in the laboratory, as the product finds extensive use in the preparation of sulphydric acid. When the quantity of material acted on is at all considerable, the reaction is sometimes very powerful and the mixture is thrown from the vessel: great care is therefore requisite. Formerly chemists supposed even volcanos to be produced by similar reactions, for which reason the name of *Lémery's volcano* was given to this preparation.

*Sesquisulphide of Iron*  $\text{Fe}_2\text{S}_3$ .

§ 787. Sesquisulphide of iron, corresponding to the sesquioxide, is obtained by decomposing hydrated peroxide of iron by sulphydric acid, at a temperature of  $212^\circ$ . This compound easily decomposes.

*Bisulphide of Iron*  $\text{FeS}_2$ .

§ 788. Bisulphide of iron  $\text{FeS}_2$ , which corresponds to no known oxide of iron, is abundantly found in nature, occurring in the form of brilliant cubic crystals, of a brass-yellow colour, and called by mineralogists *iron pyrites*, or simply *pyrites*. Pyrites are often sufficiently hard to strike fire with steel. The same product may be obtained in the laboratory, in the form of a yellow powder, by heating very finely dissolved protosulphide of iron with half its weight of sulphur, until the excess of the latter is volatilized. Its density is 4.98. Bisulphide of iron is not attacked by dilute acids, while the protosulphide, under the same circumstances, gives off sulphydric acid in abundance. Iron pyrites, subjected to the action of heat, parts with a portion of its sulphur, which distils over, while a sulphide composed of 100 parts of iron and 68 of sulphur remains, which may be considered as a special sulphide.

*Magnetic Pyrites.*

§ 789. Native sulphides of iron, of a bronze colour, are found in crystalline masses, the form of which is a regular hexahedral prism: they contain less sulphur than the bisulphide, or ordinary pyrites, and are called *magnetic pyrites*, because they affect the needle. Their composition corresponds in general to the formula  $\text{Fe}_7\text{S}_8 = 5\text{FeS} + \text{Fe}_2\text{S}_3$ .

COMPOUND OF IRON WITH NITROGEN.

§ 790. When dry ammoniacal gas is passed over fine iron-wire, heated to a dull red-heat in a porcelain tube, the metal becomes very brittle, and increases remarkably in weight, while a nitruret of iron is formed, containing 12 or 13 per cent. of nitrogen. This product is more readily obtained by heating anhydrous protochloride of iron in a glass tube, in a current of dry ammoniacal gas,

when nitruret of iron remains in the form of a metallic sponge, of a silvery whiteness.

#### COMPOUND OF IRON WITH PHOPHORUS.

§ 791. A combination of iron and phosphorus is obtained by heating a mixture of phosphate of lime and charcoal in a forge-fire, in a crucible covered with charcoal, when a very hard and brittle gray metallic lump remains, capable of a fine polish. The composition of this substance corresponds to the formula  $\text{Fe}_4\text{P}$ .

A very small quantity of phosphorous changes the qualities of iron in a remarkable manner, and renders it brittle when cold. Phosphuretted ores may do for cast-iron, but never are fit to be rolled into good bar-iron.

#### COMPOUNDS OF IRON WITH ARSENIC.

§ 792. Arsenic readily combines with iron in a great number of proportions, forming in all cases very brittle compounds, several of which are found crystallized in nature. The mineral called *mispickel* is a compound of iron with arsenic and sulphur, of the formula  $\text{FeS}_2 + \text{FeAs}_2$ , while its crystalline form is that of a right prism with a rhombic base.

#### COMPOUNDS OF IRON WITH CHLORINE.

§ 793. Two combinations of iron with chlorine, corresponding to the protoxide and sesquioxide, are known.

##### *Protochloride of Iron* $\text{FeCl}$ .

§ 794. This compound is obtained when iron filings are heated with chlorine, care being taken that the latter is not in excess, as otherwise sesquichloride would be formed. It is obtained with greater certainty in a state of purity by heating iron in a current of chlorohydric acid gas.

Protochloride of iron forms a brown fluid mass, which crystallizes on cooling: it is prepared in solution in water, by heating iron filings with chlorohydric acid and evaporating the liquid, when green crystals of the formula  $\text{FeCl} + 6\text{HO}$  are obtained.

##### *Sesquichloride of Iron* $\text{Fe}_2\text{Cl}_3$ .

§ 795. Sesquichloride or *chloride of iron* is prepared by heating iron in a current of chlorine, and volatilizing the product in this gas, when beautiful rainbow-like spangles of a brown or deep green colour are obtained. The chloride dissolves in water, yielding a yellow solution, which can be immediately obtained by treating iron with aqua regia. The solutions of sesquichloride of iron in alcohol and in ether lose their colour and precipitate protochloride of iron when exposed to the solar light.

Sesquichloride of iron is decomposed by steam at a red-heat,

when chlorohydric acid is disengaged, and on the sides of the tube in which the experiment is made small glittering spangles of sesquioxide of iron are deposited, resembling the specular oxide found in the fissures of volcanic lavas. This mineral has been supposed to have been formed in a similar manner.

#### COMPOUNDS OF IRON WITH CYANOGEN.

§ 796. Iron forms several compounds with cyanogen, particularly remarkable for their multiple combinations.

If cyanide of potassium be added to a solution of a protosalt of iron, protocyanide of iron is obtained as a white precipitate, which retains with great energy a portion of the reagent which served to produce it. It is obtained in greater purity by treating Prussian blue with sulphydric acid, when a white precipitate, which soon changes to blue in the air, is formed.

Cyanide of iron combines with a great number of other metallic cyanides, producing double cyanides, which, besides being of great technical importance, are much used in the laboratory as reagents. In these compounds the iron has lost its habitual characteristic properties, being no longer precipitated by the reagents which usually throw it down from its saline solutions or from the chlorides. The characteristic properties of the simple cyanides are also modified in such double salts, for which reason these compounds have been considered, not as real double cyanides, but as combinations of the metal with a compound electro-negative body, called *ferro-cyanogen*.

*Double Cyanide of Iron and Potassium, or Ferrocyanoide of Potassium*  $\text{FeCy} + 2\text{KCy}$ .

§ 797. This double cyanide, which is also called *prussiate of potash*, is the most important of these compounds, and is brought into commerce in the form of beautiful yellow crystals, of the formula



It contains 12.8 per cent. of water, which it readily loses on a slight elevation of temperature: 100 parts of water dissolve 25 parts of the salt at ordinary temperature, and 50 parts at the boiling point. This double cyanide is very fixed, being neither decomposable by the alkalis nor even the alkaline sulphhydrates; while the action of heat destroys the salt and evolves nitrogen, when the residue, treated with water, yields a solution of cyanide of potassium and an insoluble black substance, which is a true carburet of iron, of the formula  $\text{FeC}_2$ .

This salt is prepared on a large scale by fusing carbonate of potassa with animal charcoal, which must be prepared expressly from animal matter containing but few phosphates. Calcined bone, dried flesh, skins, and principally old shoes are used for its

preparation: these substances leave a carbonaceous residue, highly charged with nitrogen, which is afterward heated with about its own weight of carbonate of potassa, in large cast-iron kettles into which the smoky flame of a reverberatory furnace enters. The carbonate of potassa is first fused alone, and then the animal charcoal is added, when a reaction takes place accompanied with effervescence, and the mass is continually stirred with iron rods. Cyanide of potassium and cyanide of iron are formed, the iron being furnished by the sides of the kettle and the rods; and when the reaction is ended, the matter is removed and treated with boiling water. The hot solution is filtered, and evaporated to crystallization; while the mother liquid, on being again concentrated, still yields crystals, which, with the former ones, are purified by dissolving them in boiling water and allowing the liquid to cool slowly.

Within a few years, cyanide of potassium has been prepared by the direct combination of carbon with nitrogen, in the presence of carbonate of potassa; and this process is now applied to the manufacture of prussiate of potash on a large scale. Wood charcoal, impregnated with a concentrated solution of carbonate of potassa, is heated to a high temperature in brick vent-holes, in a current of hot air which has been deprived of its oxygen by passing over a long column of burning coke. From time to time the portion of potashed charcoal at the lower part of the holes is withdrawn, and additional charcoal is introduced through the upper opening to keep the supply constant. The alkaline charcoal, in this operation, is exposed for 10 hours to the action of nitrogen, and then is heated in an iron boiler, with water and finely powdered sparry iron. The liquid yields when evaporated beautiful crystals of very pure prussiate of potash, while the residue of the charcoal is again soaked in a concentrated solution of carbonate of potassa and the operation recommenced.

The solution of prussiate of potash, added to the solutions of a great number of metallic salts, affords precipitates which are often remarkable for their brilliant colours, and serve as distinguishing characters of the metals. In these double decompositions, the cyanide of potassium alone is decomposed, by being changed into a cyanide of the metal which exists in the reacting solution, while this new cyanide combines with the cyanide of iron. If prussiate of potash  $\text{FeCy} + 2\text{KCy}$  be added to a solution of sulphate of copper  $\text{CuO}, \text{SO}_3$ , a characteristic reddish-brown precipitate, of the formula  $\text{FeCy} + 2\text{CuCy}$ , is obtained. The prussiate, poured into a solution of sulphate of zinc  $\text{ZnO}, \text{SO}_3$ , gives a white precipitate  $\text{FeCy} + 2\text{ZnCy}$ . A series of compounds of similar formulæ, all of which contain protocyanide of iron, is thus obtained.

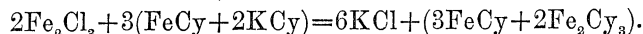
The formula of the precipitate obtained with a salt of lead is  $\text{FeCy} + 2\text{PbCy}$ , which, by treatment with sulphydric acid, forms an



insoluble sulphide, and an acid liquid which yields white crystals when evaporated under cover near a saucer filled with concentrated sulphuric acid. These crystals are formed by a real hydracid  $\text{FeCy} + 2\text{HCy}$ , called *ferro-hydrocyanic acid*, or *hydrocyano-ferric acid*, or *ferro-cyanhydric acid*, the solution of which is inodorous and possesses none of the properties of hydrocyanic acid. The double cyanides may therefore be regarded as *ferrocyanides*.

Prussiate of potash yields a white precipitate with protosalts of iron, composed for the greater part of protocyanide of iron, but always retaining a certain quantity of alkaline cyanide. This precipitate soon changes in the air.

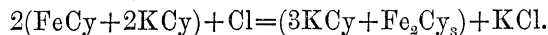
With the salts of peroxide of iron, prussiate of potash gives a beautiful blue precipitate, called Prussian blue, which is used in dyeing and in oil-painting. The following reaction ensues between perchloride of iron and prussiate of potash:



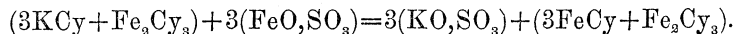
The formula of Prussian blue is  $3\text{FeCy} + 2\text{Fe}_2\text{Cy}_3$ .

§ 798. If a current of chlorine be passed through a solution of prussiate of potash and the liquid boiled, a green precipitate is formed, which, when heated with chlorohydric acid, gives off a certain quantity of mixed oxides of iron, and leaves a green residue, of the formula  $\text{FeCy} + \text{Fe}_2\text{Cy}_3 + 4\text{HO}$ . It is a compound resembling magnetic oxide, if the water of combination be overlooked.

§ 799. If the current of chlorine be stopped at the moment when the solution no longer throws down a blue precipitate of sesquisalts of iron, a liquid, yielding beautiful red crystals on evaporation, is obtained. It is important not to prolong the action of the chlorine too much, and to keep the liquid constantly agitated. The solution is frequently tested with a sesquisalt of iron, and the current of chlorine is arrested as soon as a precipitate is no longer formed. It is also well to neutralize the liquid gradually with a little potassa. The red salt, which has been called *cyanoferride* or *ferricyanide of potassium*, has the formula  $3\text{KCy} + \text{Fe}_2\text{Cy}_3$ ; and contains no water of crystallization. The reaction from which it originates is the following:



The red prussiate is much less soluble than the yellow, 38 parts of cold water being required to dissolve 1 part of it. Protosalts of iron yield with red prussiate of potash a beautiful blue precipitate of the formula  $3\text{FeCy} + \text{Fe}_2\text{Cy}_3$ , the reaction being as follows:



Red prussiate of potash yields with salts of lead a precipitate  $3\text{PbCy} + \text{Fe}_2\text{Cy}_3$ , which gives, when treated with sulphuric acid, a precipitate of sulphate of lead and a compound  $3\text{HCy} + \text{Fe}_2\text{Cy}_3$ ,

called *hydro-ferricyanic acid*, which dissolves with a red colour. The solution, when evaporated, deposits the salt in yellowish-brown crystals.

#### COMPOUNDS OF IRON WITH CARBON.

§ 800. Iron combines with carbon when in presence of this substance, at a very high temperature. It has been shown (§ 795) that a carburet of iron  $\text{FeC}_2$  is obtained by decomposing prussiate of potash by heat: by the direct combination of iron with carbon, compounds so rich in carbon are never obtained, as the most carburetted products only contain about 5 per cent. of carbon, their composition resembling the formula  $\text{Fe}_4\text{C}$ . These carburetted irons are called *cast-iron*, which is again divided into *white cast-iron* and *gray cast-iron*.

Iron, heated in blast-furnaces at a very high temperature in contact with charcoal, passes into the state of cast-iron, which, by cooling suddenly on leaving the furnace, forms hard and brittle metallic masses, whiter than the soft iron, and consisting of *white cast-iron*. If, on the contrary, the iron be cooled slowly, the carbon which was in combination with the iron separates by crystallization, forming an infinite number of small black graphitose spangles, which impart a deep gray colour to the mass. The small spangles of carbon are scattered through the iron, the greater part of which is decarburetted, and such iron, which is called *gray* or *soft cast-iron*, is much more malleable than the white sort, and can be cut with a file.

All kinds of cast-iron do not lose their combined carbon with equal readiness; when the iron-ore contained phosphorus or sulphur, the metal retains the character of white cast-iron, even after a very slow cooling. Certain kinds of cast-iron, which contain manganese in combination, possess also the property of retaining their combined carbon, and present, after cooling, a crystalline fracture, with very large brilliant laminae, which intersect each other at angles of  $120^\circ$ ; hence the crystalline form is inferred to be a regular hexahedral prism.

This iron is called *lamellar cast-iron*, and is obtained from the manganiferous sparry ores (§ 782).

When white cast-iron is treated with chlorohydric acid or dilute sulphuric acid, the metal dissolves with evolution of hydrogen gas, but at the same time a volatile oil of a nauseous smell is generated, resulting from the combination of the hydrogen with carbon in the nascent state. If, on the contrary, gray cast-iron is dissolved, a certain quantity of this oil is produced, by the combination of hydrogen with the portion of carbon which was in combination with the iron, while the free carbon remains in the form of small crystalline spangles.

Cast-iron, under certain circumstances, assumes an intermediate

state between the gray and white, when, the separation of graphite not taking place throughout the whole mass, but only in some portions, the substance presents the appearance of white cast-iron, more or less spotted with gray. This kind is called *spotted* or *mottled cast-iron*, (*fonte truitée*.)

#### COMPOUND OF IRON WITH SILICIUM.

§ 801. A compound of iron with silicium is obtained by heating in a crucible covered with damp charcoal a mixture of iron filings, silicic acid, and charcoal, in a forge-fire, when a fused metallic lump, possessing a certain degree of malleability, is formed. Iron can combine, in this case, with 9 or 10 per cent. of silicium. Cast-iron, particularly that made in blast-furnaces at very high temperatures with coke, generally contains 1 or 2 hundredths of silicium.

#### DETERMINATION OF IRON, AND ITS SEPARATION FROM THE METALS PREVIOUSLY DESCRIBED.

§ 802. In chemical analyses iron is nearly always determined in the state of sesquioxide, and when it exists as such in its solutions is precipitated by ammonia or carbonate of ammonia. It is best to make the precipitation in a hot liquid, as the hydrated sesquioxide is then less gelatinous and more easily washed on the filter. When the iron exists in the state of protoxide, it must be converted into sesquioxide by evaporating the liquid with nitric acid, or by passing a current of chlorine through it; in which latter case the excess of chlorine must be driven off by boiling. Sesquioxide of iron is then precipitated by ammonia. The superoxidation of the iron may also be affected by adding chlorohydric acid, and then a small quantity of chlorate of potassa, to the liquid, when, by boiling, the chlorohydric acid and chlorate of potassa mutually decompose each other, while chlorine is set free, which produces the superoxidation of the iron. Frequently it is preferable to precipitate sesquioxide of iron by succinate of ammonia, which throws it down more completely than ammonia, as an excess of this last reagent may redissolve a small quantity. The precipitate of sesquisuccinate of iron is decomposed by heat, leaving pure peroxide of iron.

In some cases, sesquioxide of iron must be precipitated with caustic potassa in excess; but the precipitate then retains a small quantity of potassa with great obstinacy, and is freed from it only by boiling several times with distilled water. When the precipitate is copious, it is better, after having collected it on the filter and washed it with a small quantity of hot water, to redissolve it in weak chlorohydric acid, saturate the liquid by ammonia, and precipitate again with succinate of ammonia.

When the solution contains organic substances, such as sugar, tartaric acid, etc., ammonia no longer precipitates sesquioxide of iron, nor does even carbonate of ammonia; and the iron must then

be precipitated as sulphide by sulfhydrate of ammonia. The precipitate is collected on a filter, and washed with water, to which a small quantity of sulfhydrate of ammonia is added, in order to prevent the sulphide of iron from being converted into sulphate by contact with the air; after which the precipitate is redissolved in chlorohydric acid, the iron brought to the state of peroxide, either by means of chlorine or by evaporating the solution with a small quantity of nitric acid, and the sesquioxide formed is then precipitated by succinate of ammonia.

§ 803. In order to separate the alkaline metals, ammonia or succinate of ammonia is used after the iron has been brought to the state of sesquioxide. It is separated from the alkalino-earthly metals by the same reagents, care being taken at the same time that the ammonia contains no carbonate, or cannot absorb carbonic acid from the air, as the carbonate of ammonia formed would cause the precipitation of the earths. When iron is to be separated from magnesia, a quantity of sal ammoniac sufficient to prevent the magnesia from being precipitated by an excess of ammonia must be added to the liquid; but the latter, most frequently, already contains free acid enough to produce the quantity of ammoniacal salt necessary during its saturation by ammonia.

In order to separate iron from alumina, the iron is first brought to the state of sesquioxide, if it does not already exist in that state, and then an excess of caustic potassa is added; when, by boiling the liquid for some time, all the alumina dissolves in the potash, leaving only the sesquioxide of iron as a precipitate. The filtered alkaline liquid is then supersaturated with chlorohydric acid, and the alumina precipitated by an excess of carbonate of ammonia.

The separation of iron and manganese is easily effected when the iron exists as sesquioxide, and we have seen that it can always be readily brought to that state. The manganese, moreover, is always present as a protosalt; for the other salts of manganese, not being very fixed, are soon converted by ebullition into protosalts. The same process as described for the separation of sesquioxide of iron from magnesia is adopted; that is, a quantity of ammoniacal salt sufficient to prevent the precipitation of the oxide of manganese is added to the liquid: generally, however, the ammonia necessary to saturate the acid liquid is sufficient to produce the ammoniacal salt required. The sesquioxide of iron is then precipitated by ammonia or succinate of ammonia, and the manganese is obtained from the filtered liquid by sulfhydrate of ammonia as sulphide.

When a solution of a sesquisalt of iron is precipitated by ammonia or carbonate of soda, changes of colour are observed, which may guide the operator in the separation of the iron, and allow the iron and other metals which exist in the liquid to be successively precipitated. The sesquisalts of iron, dissolved in an acid liquid, are

of a very pale yellow colour, and when ammonia or carbonate of soda are added by small quantities at a time, the liquid becomes more and more deeply coloured as it approaches saturation, and at last assumes a deep brown colour before any deposit is formed. If it is then subjected to ebullition, the peroxide of iron is completely precipitated: the liquid is bleached, retaining still all the oxides of the formula  $RO$  in solution, which are much more powerful bases than sesquioxide of iron, and, in general, than the oxides of the formula  $R_2O_3$ . In order to make the separation properly, the liquid is first heated to boiling, and the ammonia or carbonate of soda then added, stirring it continually, and discontinuing when the liquid has turned brown. It is then boiled for some time, when a brown precipitate of hydrated sesquioxide of iron is generally formed. If the liquid is not discoloured, a few drops of the reagent are added, it is again boiled, and this is continued until discoloration takes place. It is then filtered while boiling, and a considerable quantity of carbonate of soda is added to effect the precipitation of the other metallic oxides which exist in the solution. There is, therefore, a considerable interval between the moment of the complete precipitation of the oxides of the formula  $R_2O_3$ , and that of the commencement of the precipitation of the oxides  $RO$ .

In this way, sesquioxide of iron may be separated with a considerable degree of accuracy from all protoxide with which it is mixed in the liquid; but the admission of air must be avoided as much as possible, as its oxygen would convert a portion of the protoxide into sesquioxide. It is often necessary, in the analysis of mineral substances, to determine the relative proportions of the sesquioxide and protoxide of iron they contain, which can be done exactly when the mineral dissolves readily in non-oxidizing acids, such as chlorohydric. The material is finely powdered, and treated in a small flask with hot concentrated chlorohydric acid, the liquid being continually boiled, in order that the steam disengaged may prevent the admission of air into the flask; and the boiling is continued until the greater part of the acid in excess is evaporated. It is then treated with boiling water, and the sesquioxide precipitated by carbonate of soda, added by drops, avoiding as much as possible the contact of the air. When the liquid is deprived of colour, it is allowed to rest for some time in the flask, which is corked: the clear liquid is decanted, collected rapidly on a filter, and washed with boiling water. The filtrate contains the protoxide of iron, which is brought to the state of sesquioxide by means of chlorine, and precipitated by an excess of carbonate of soda.

§ 804. It is, however, difficult to prevent a portion of the protoxide of iron from changing into sesquioxide by absorption of the oxygen of the air. Greater exactness is obtained by another process, which may be applied to various other cases. If a solu-

tion of permanganate of potassa be added to a solution of a proto-salt of iron, the permanganate immediately loses its colour, by being decomposed into protoxide of manganese and potassa, which base combines with the acid, and into oxygen, which converts the protoxide of iron into sesquioxide.\* The discolouration of the permanganate of potassa takes place as long as any protoxide of iron remains in the liquid; but as soon as all the protoxide is changed into sesquioxide, the smallest drop of the solution of permanganate of potassa gives the liquid a very decided red tinge. If the solution of permanganate of potassa is of standard quality, it suffices to measure exactly the quantity necessary to produce a permanent red colour, and the quantity of iron which existed in the state of protoxide can thence be directly inferred.

The permanganate of potassa used to make the standard solution is prepared by heating, for two hours, in an earthen crucible, a mixture of 2 parts of binoxide of manganese, 3 parts of caustic potassa, and 1 part of chlorate of potassa.† The mass is broken to pieces after cooling, treated with 3 or 4 times its weight of water, and the liquid filtered through asbestos or powdered glass, to separate the sesquioxide of manganese. Weak nitric acid is then added until the liquid assumes a beautiful violet-red colour. The solution is preserved in a well-corked bottle, as it would be soon changed by the particles of organic dust floating in the air.‡

In order to determine the standard of the solution, 1 gramme of highly-polished piano-forte wire, exactly weighed, is dissolved in 25 cubic centimetres of chlorohydric acid, and the liquid diluted with water recently boiled, so as to increase its volume to about 1 litre.§ Again, 100 divisions of the solution of permanganate of

\* The solution must necessarily contain free acid enough to dissolve the oxide of manganese formed.—*W. L. F.*

† Another proportion, given by Gregory, is as follows:—8 parts of peroxide of manganese, 10 parts of caustic potassa, and 3 parts of chlorate of potash. But the best method, as the only one by which permanganate of potassa can be obtained in crystals and free from chloric acid, according to Liebig, is by igniting pure peroxide of manganese with a fixed alkali, with access of air.—*W. L. F.*

‡ The use of permanganate of potassa as a means of determining iron in any case has been objected to by many chemists, on the ground that a standard solution would not keep uniform for any length of time. This objection is unfounded; for a solution made by dissolving crystals of the salt remained perfectly unaltered for a period of six months, during which time it was often tested. The solution must, however, be kept in a bottle with a tight-fitting ground-glass stopper, and the bottle ought always to be kept as full as possible. The manganate should be converted into permanganate, rather by adding a quantity of boiling water to its concentrated solution than by introducing nitric acid.—*W. L. F.*

§ As not even piano-forte wires consist of pure iron, it is better to employ a protosalt at once: of these the protosulphate of iron and ammonia is most commendable, as being least of all subject to decomposition, and easy to prepare. Of this salt, 6.429 gm., which correspond exactly to 1 gm. of metallic iron, are dissolved, and the solution having been made acid, the permanganate may be immediately added.—*W. L. F.*

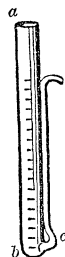


Fig. 477. potassa are introduced into a graduated alkalimeter (fig. 477), and poured from it into the vessel B (fig. 478), which contains the protochloride of iron, stirring constantly to facilitate the mixture. The solution of the permanganate is added, by small quantities at a time, until the liquid assumes a permanent roseate tinge. The number of divisions and fractions of a division necessary to produce this result are noted down: supposing this number to be 75.5 div., the conclusion will follow that 75.5 div. of the solution of permanganate correspond to 1 gramme of protoxide of iron, and consequently that 1 div. of permanganate corresponds to 0.01325 gr. of metallic iron.\*

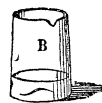


Fig. 478. This being done, in order to analyze a substance containing protoxide and sesquioxide of iron at the same time, 1 gramme of it is dissolved in chlorohydric acid, the liquid is diluted with boiled water until it occupies the volume of about 1 litre, and then the standard solution of permanganate of potassa is carefully added until the liquid assumes a roseate tinge. Let us suppose that to produce this effect, 22.0 div. of the solution of the permanganate were required; the gramme of the substance subjected to analysis will then contain  $22.0 \times 0.01324$  gr., or 0.291 gr. of iron, existing in the state of protoxide, or, lastly, 0.374 gr. of protoxide of iron.

The quantity of sesquioxide can readily be determined by the same process:—1 gramme of the substance is again dissolved in concentrated chlorohydric acid, and then 4 grammes of sulphite of soda, dissolved in a small quantity of water, are poured into the solution gradually and by small quantities. The sulphurous acid which is set free by the reaction of the chlorohydric acid on the alkaline sulphite converts the perchloride of iron into protochloride, so that all the iron in the substance then exists in the solution as protochloride. The liquid is boiled to drive off the excess of sulphurous acid, diluted with water to about the volume of 1 litre, and the standard solution of permanganate is added. Supposing that it was necessary to add 36.0 div. of the alkalimeter, in order to obtain a permanent rose-colour, the conclusion follows that the substance contains  $36.0 \times 0.01324$  gr., or 0.477 of metallic iron. Now, as it has been already found to contain 0.291 of iron in the state of protoxide, there are 0.186 gr. present in a more highly oxidized state, corresponding to 0.266 gr. of sesquioxide.

\* The result will be the more exact the more dilute a solution of permanganate of potassa is employed, and the accuracy of the determination may, in fact, be carried to almost any degree.—*W. L. F.*

## METALLURGY OF IRON.

§ 805. The only ores of iron employed are the oxides and the carbonate; while the sulphides, although very abundant in nature, are not used for the extraction of iron, as the process would be too expensive, and, besides, a metal of inferior quality would be obtained. The principal ores which are worked are—

1. The magnetic oxide, found in considerable masses in the old rocks, principally in the micaceous schists,\* in which well-defined octahedral crystals are often found scattered, is generally a very rich ore, affording iron of excellent quality: the greater portion of Swedish iron is procured from it.

2. The anhydrous peroxide of iron, which is found in some transition rocks, and in the secondary rocks, in large masses, resembling sometimes real strata. The oxide, in this case, is amorphous, and is called *red hematite*. It also constitutes veins in the old rocks, as at Framont, in the Vosges. This ore is used in many of the foundries in the north of Germany.

Specular iron is generally found in veins, but rarely in sufficient quantity for foundry use. It also forms considerable masses in the old rocks, a most remarkable example of which is the deposit in the island of Elba.†

3. Hydrated peroxide of iron, which is found in the transition rocks, or at the junction of the transition and secondary rocks, in the form of concrete brown masses, when it is called *brown hematite*. In France, the foundries in the Pyrenees use this ore.

4. Hydrated peroxide of iron, which is also found in small concrete grains, and is called *granular iron ore*. It forms deposits A

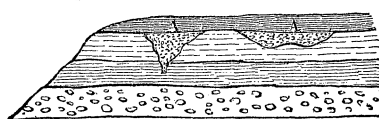


Fig. 479.

(fig. 479) at the time of separation of certain strata of the jurassic rocks, but more frequently in the middle tertiary rocks, covering the layers of jurassic limestone and chalk.

The size of the grains varies from that of a pea to that of a millet-seed. The majority of the foundries in the middle of France, and in Champagne and Berry, smelt this ore.

An ore is also found in certain stages of the jurassic rocks, consisting of small grains of hydrated peroxide of iron, adhering

\* A mistake has here crept into the text; magnetic oxide being seldom or never found in micaceous schists, but occurring in abundance in talcose and chloritic schists, and in serpentine; while the largest masses of it are found in various igneous rocks of a more recent origin, especially in basalt and dolerite.—W. L. F.

† At the Serra da Piedade and the Pico da Itabira, both in Brazil, specular iron occurs in such quantity as to form a peculiar species of rock, called itabirite, of a dense and slaty character.—W. L. F.



firmly to each other, and forming real strata; and this ore, from its resemblance to the eggs of fish, is called *oolithic ore*.

5. Sparry iron, or crystallized protocarbonate, sometimes mixed with considerable proportions of carbonate of manganese, which is found in veins in the old and transition rocks. It sometimes also accompanies the brown hematites which are met with at the line of separation of the old and transition rocks. This ore, smelted with charcoal, yields laminated cast-iron, which is used for manufacturing steel.

6. In the argillaceous strata of the coal-fields, flattened nodules of carbonate of iron, mixed with clay, are frequently found, and are sometimes very rich in iron, constituting an ore the more valuable because it is found in the midst of fuel, and is easily extracted. This ore is very abundant in England.

7. Lastly, an iron-ore is found in some low places, immediately beneath the soil, consisting of hydrated peroxide, mixed with phosphate. This ore yields phosphorous cast-iron, the use of which is limited. It is called *bog ore*.

Iron is sometimes found in the native state, forming often very large compact masses, which are never in place, but have fallen from space as aerolites. This iron, which is never pure, being always more or less mixed with nickel, is often scattered through a grayish stone, the surface of which appears to have undergone an incipient fusion. These masses are called *meteoric stones*, *aerolites*, or *meteorolites*. Probably, a great number of such meteors circulate in space, influenced by the same forces which maintain the planets in their orbit, and fall to the surface of the earth when, by virtue of their motion, they approach near enough to this planet to be acted on by the attraction of the latter. Sometimes meteoric iron possesses all the qualities of malleable iron, and cutting-instruments even have, for sake of curiosity, been made of it.

§ 806. Iron ores are never subjected to any complicated preliminary operations. The granular ores are generally held together by a clay, very poor in oxide of iron, and easily removed by washing (§ 735).

Other ores often require a preliminary roasting, which renders their smelting more easy, by driving off the water, and carbonic acid, if the ore is carbonated, and acting especially by disaggregating the ore, and rendering it porous and more friable.

§ 807. We have seen (§ 766) that the oxides of iron are very easily reduced when heated in a current of hydrogen: their reduction is also effected under the same circumstances by carbonic oxide gas. It may hence be supposed that the reduction of oxide of iron in ores is not very difficult; but then the metallic iron formed is still intimately mixed with the gangue, which prevents its particles from uniting together. If the gangue were very

fusible, it would be sufficient to heat the ore to a degree sufficient to fuse the former, and by then hammering this metallic sponge, the particles of iron would unite together, while the gangue would be pressed out in the form of scoriæ. But, if the gangue fuses with difficulty, it would melt only at the temperature at which the iron, in contact with charcoal, is converted into cast-iron, and we should no longer obtain malleable, but cast-iron. Now, the ordinary gangue of iron-ore being quartz or clay, which are two nearly infusible substances, two processes are adopted to fuse them. If soft iron is to be obtained immediately from very rich ores, the latter are heated with charcoal, when the gangue, combining with a portion of the unreduced oxide of iron, forms a very fusible double silicate of alumina and protoxide of iron. A very high temperature, therefore, is not required; the iron does not pass into the state of cast-iron, and it suffices to hammer the spongy metal to unite it together and press out the scoriæ. But a quantity of oxide of iron, proportioned to the quantity of gangue in the ore, is necessarily lost, for which reason this process can only be adopted in the case of very rich ores.

If, on the contrary, the iron is to be extracted completely from the ore, the silicate of alumina must be made fusible by giving it another base than oxide of iron. The only base which can be economically substituted is lime; but as the double silicate of alumina and lime is much less fusible than that of alumina and iron, a high temperature is required, and the iron passes into the state of cast-iron, which liquifies at the same time with a double silicate, or *slag*.

As may be seen, the results of these two methods are very different. The first is used only in a few places, as it requires rich and very pure ores, and consumes an immense quantity of fuel. It is adopted in the Pyrenees, and known as the *Catalan method*.

#### TREATMENT OF IRON-ORE BY THE CATALAN METHOD.

§ 808. The Catalan forge consists of a crucible, or *hearth*, made by a quadrangular cavity U (figs. 480 and 481), of about 0.7 m. in depth, and supported by one of the walls of the forge. The crucible is built in solid mason-work of dry stones, fastened together with clay. The part of the mason-work occupied by the crucible does not rest immediately on the ground, but on several small arches, which prevent the dampness from penetrating the crucible and deranging the hearth. Above the arches is a layer of scoriæ and clay, covered by a granite slab, which forms the bottom, or the *floor* of the hearth.

The four lateral faces of the crucible rise above the bottom stone.

VOL. II.—F

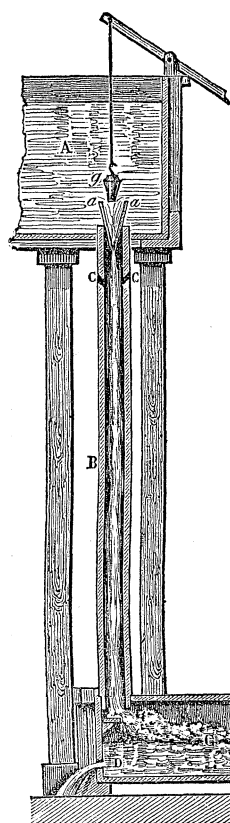


Fig. 480.

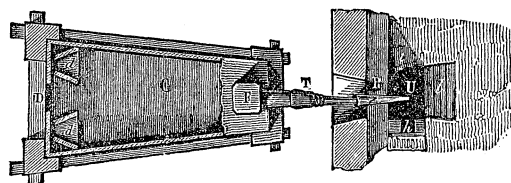


Fig. 481.

The front face *h* is called the *chio*, or floss-hole.

The opposite face *i* is called the *cave*.

The left one *R* is called the *porges*.

Lastly, the right face *l* is called the *ore* or *contrevent*.

The face of the *chio*, which presents a vertical surface of about 0.65 m., is formed by three pieces of iron placed end to end, the two extreme ones of which are called *latai-roles*; that in the middle, the *restanque*, serves as a *point d'appui* for the levers, or *fire-irons*, with which the workmen raise the mass of iron formed during the process.

The left face, the *porges*, is vertical, and composed of pieces of iron *t, t, t* (fig. 483) laid endwise upon each other.

The right face, the *ore* or *contrevent*, is composed of pieces of iron *s, s, s* (fig. 483), which are

wedge-shaped, and slightly inclined, being so arranged that their surface forms a curve.

The *cave i*, which consists wholly of mason-work, fastened with clay, is slightly inclined outward to 5° or 8°.

The *twyer Z*, which conveys the blast into the furnace,

rests on the upper piece of the *porges*, and is made of a conical piece of copper, the edges of which are merely brought together without soldering. The position of the *twyer* exerts great influence over the operation: its inclination varies from 35° to 40°. The wind is conveyed from the bellows into the *twyer* through a copper nozzle *T*, fastened to the wind-trunk *G* of the bellows by a leather tube.

The depth of the Catalan furnace is about.....	0.7m.
Its average width, from the chio to the cave.....	0.6
Its average width, from the porges to the lower part of the contrevent .....	0.7
Its average width, from the porges to the upper part of the contrevent .....	1.0

The bellows of the Catalan forges of Ariège is called a *trumpet*, (trompe,) and is composed of—

1st. An upper basin A (fig. 481), fed by spring-water.

2d. Two pipes B, of about 6 metres in height, formed by trees hollowed out, and crossing the bottom of the basin A.

3d. A lower box C, having two openings, one at D below, the other above at E, to which is fitted a tube EF, terminated by the wind-trunk G.

The upper opening of the tubes B is contracted by the boards *a* which are supported by bars. The aperture formed by the lower part of the boards is called the *étranguillon*, on a level with which the sides of the tubes are pierced with inclined holes *c* *c*, called *breathing-holes*, (aspirateurs.) Lastly, the tubes enter the upper wall of the box C, and open at a small distance above a bench *d*.

The water of the upper basin A, passing through the etranguillon into the vertical pipes B, carries with it the external air, which in this way passes through the openings *c c*. The water breaking over the bench escapes through the lower orifice D, while the air passes out by the nozzle G. The position of the boards forming the etranguillon is regulated by wooden wedges *g*, which, being fixed to the end of a jointed lever, which a man works by a chain at the bottom of the forge, is elevated or depressed in order to obtain the quantity of air necessary for the various stages of the operation.

The *beetle*, or *tilt-hammer*, used in forging iron, represented in fig. 482, consists of a cast-iron face P, weighing about 600 kilogs., mounted on a helve of beech-wood, and secured by iron bands, while the gudgeons on which the hammer turns are fastened to a cast-iron piece H fixed to the helve.

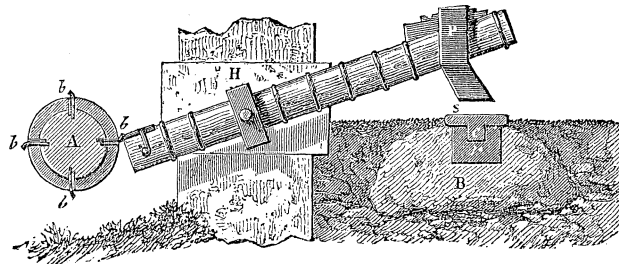


Fig. 482.

The hammer is raised by means of iron cams *b, b, b* on the water-wheel A.

The iron anvil S is fastened by a tenon *c* to a piece of cast-iron *r*, which is itself solidly set by means of wooden wedges into a large block of wood, or a piece of granite, B. In order to accelerate the fall of the hammer, which should strike from 100 to 125 blows per minute, a stone on which the heel strikes is placed under the latter.

§ 809. These general arrangements of the forge being understood, let us now examine it in operation.

We shall suppose that the mass or *stack* of the preceding operation has been removed from the furnace to be forged under the hammer; and that the workmen are therefore occupied in getting up the fire for another smelting. For this purpose they withdraw from the hearth the hot coals which are still there, detach from the bottom and sides the adhering slag, and return the hot coals to the hearth, which is thus filled as high as the twyer. A workman divides the hearth into two parts, by a shovel which he places vertically and parallel to the porges, so that the division between the shovel and the porges shall be double of that between the former and the contrevent. Other workmen heap charcoal in the division between the shovel and the porges, and ore, broken to the size of a walnut, between the shovel and the contrevent. The shovel is gradually raised, as the space below is filled, and a wall of ore is

thus formed rising to about 0.2 m. above the contrevent. The ore is spread so as to form a saddle-back *dfg* (fig. 483), of which the edge *f* rests on the one side against the cave, and on the other on the bench of the chio.

The surface *fg* is covered by a layer of *brasque*, (damp charcoal,) well heaped up, while the space M, comprised between the wall of ore and the furnace, is filled with charcoal.

The furnace being thus charged, the blast is admitted, at first slowly, and then its force is increased. The ore is thus gradually reduced; while the workmen take advantage of this period to forge into bars the stack of the

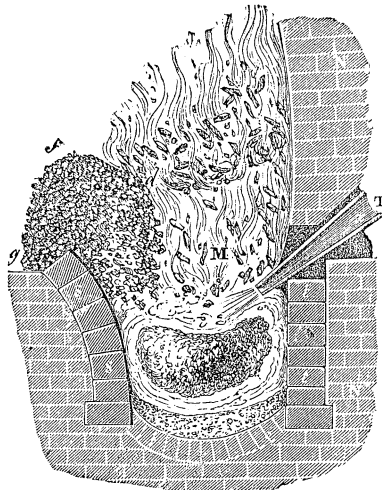


Fig. 482.

preceding operation, which they have divided into four parts, as we shall presently see. To do this, they heat these masses of iron in the furnace, by placing them in the middle of the burning char-

coal in the space M above the twyer. When they are sufficiently heated, they are removed and forged.

As the charcoal diminishes, fresh fuel is added, and small ore, called *greillade*, which is made by the breaking of the ore as it comes from the mine, is thrown in, being slightly moistened with water, to prevent it from falling too easily between the interstices of the charcoal.

Influenced by the wind projected through the twyer, the charcoal burns to carbonic acid in the space near the twyer, while farther off the carbonic acid is reduced, by the charcoal in excess, into carbonic oxide gas, the greater part of which, being obliged to pass through the highly heated ore, reduces the oxide of iron to the state of metallic iron. But the whole of the oxide is not reduced, as a portion, remaining in the state of protoxide, combines with the gangue of the ore, forming a very fusible compound silicate, a large portion of which runs off and collects in the bottom of the hearth, whence it is removed by a small opening in the chio.

In two hours, the *greillade* which falls with the fuel has deposited a certain quantity of iron at the bottom of the hearth, and the workman then commences the formation of the *mass*. He increases the draught of air, and, by carefully introducing a bar between the ore and the contrevent, draws that ore which seems more advanced near to the twyer, and adds at the same time another charge of charcoal and *greillade*.

Five hours after the commencement of the operation the ore has entirely fallen into the hearth, and the workman endeavours to unite the various fragments of spongy iron.

During the last hour of the process, the workmen break the ore under the forge-hammer, and then sift it, in order to separate the pulverulent material constituting the *greillade*, of which we have spoken.

They then remove the mass from the furnace and carry it to the hammer, where the liquid scoriæ are pressed out, and the spongy iron is rendered more compact. The mass is then, by means of a long iron wedge, divided into two equal parts, called *massoques*, which are hammered into long parallelopipedons, and again cut into two equal parts. Four pieces of iron, called *massoquettes* are thus obtained, which are rolled into bars in the first stage of the succeeding operation.

A smelting by the Catalan method generally lasts 6 hours, producing 140 to 150 kilogs. of merchantable iron, from 470 kilogs. of ore and about 500 kilogs. of charcoal.

The direct extraction of iron in the state of ductile metal is now performed only in the Pyrenees, Corsica, and a few provinces of Spain, the greater portion of iron being obtained by means of blast-furnaces, in which the metal is separated from its ores, as perfectly as possible, by using a very high temperature, at which the iron

combines with a certain quantity of carbon, forming a much more fusible compound than ductile iron.

#### TREATMENT OF IRON-ORES IN THE BLAST-FURNACE.

§ 810. The blast-furnace (fig. 484) is composed of two truncated cones C, B, united at their bases. The upper cone C, called the *belly*, (cuve,) is made of an inner lining *ii'* of refractory bricks, surrounded by a stratum of scoræ, or broken slag, which separates it from a second brick lining *ll'*, built against an outer wall *pp'*, *qq'* of cut stone or common brick, constituting the main part of the blast-furnace. The upper opening G of the belly is called the

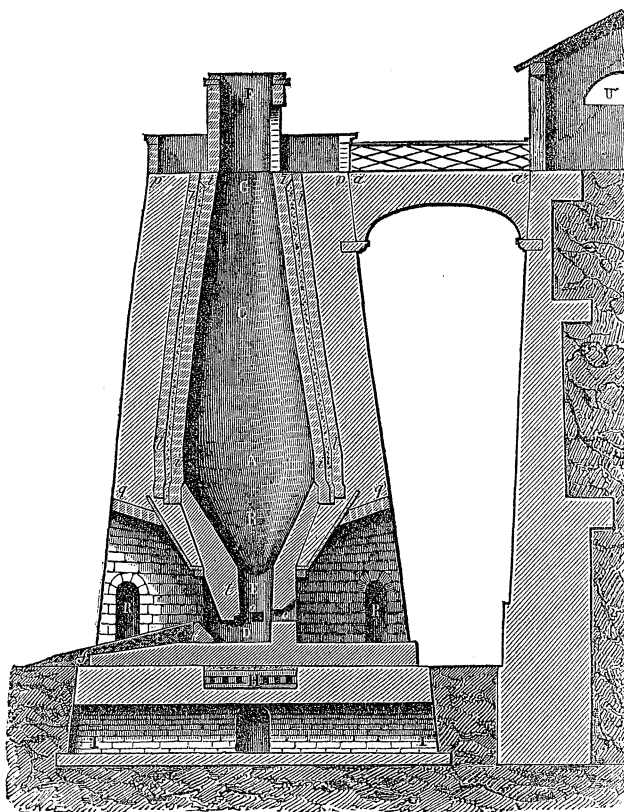


Fig. 484.

*tunnel-head*, (gueulard,) and is surmounted by a chimney F, having one or several doors, through which the charges are introduced. The lower cone B, called the *boshes*, (etalages,) is generally made of quartzose stones difficult of fusion, and which must be very

carefully selected, as on them the duration of the furnace greatly depends. In some furnaces the boshes are made of refractory bricks. They are sometimes joined to the belly by a cylindrical union or curve A, in order to avoid a re-entering angle.

Below the boshes is a prismatic space E, called the *top of the hearth*, made of refractory stones, (*fire-stone*.) Three of its sides descend to the bottom of the furnace, or the *crucible* D, while the fourth *t* stops at a few decimetres above the bottom: this side, which is called the *t ymp-plate*, is supported by strong pieces of iron let into the side-walls of the hearth.

The bottom of the hearth is formed of a quartzose stone, beneath which are openings to allow the air to circulate freely below the furnace; and, in order to prevent the accumulation of water, which would cool the hearth, and even give rise to serious accidents, the main body of the blast-furnace is built on arched galleries II. Three of the walls of the crucible are merely prolongations of its sides, while the fourth is formed by a prismatic stone *d*, called *dam-stone*, and which is slightly in front of the *t ymp-plate*; so that the anterior part of the hearth has an opening between the dam-stone and the *t ymp-plate*. We shall call that part of the furnace on which the dam-stone and *t ymp-plate* rest the *anterior part*; the opposite will therefore be the *posterior part*, and the other two the *sides*.

The posterior part and two sides have lateral openings *o*, called the *tuyeres*, or *twyers*, through which the pipes which convey air enter the furnace: these openings are on the same horizontal plane, a little above the lower edge of the *t ymp-plate*.

To assist the workmen, four niches, allowing them to approach the *twyers* and hearth, are made in the main body of the furnace, while lateral galleries R permit them to walk more freely around the furnace and to examine the *twyers*. The arrangement of the *twyers* and the pipes which convey the air from the blast-machine is seen in fig. 485, which represents a horizontal section of the furnace at the height of the *twyers*. Each wind-trunk has a register or valve, to regulate the quantity of air admitted.

The blast-furnace is generally built, when practicable, against a hill (fig. 484), and strengthened by mason-work. A terrace is made, at the height of the mouth,

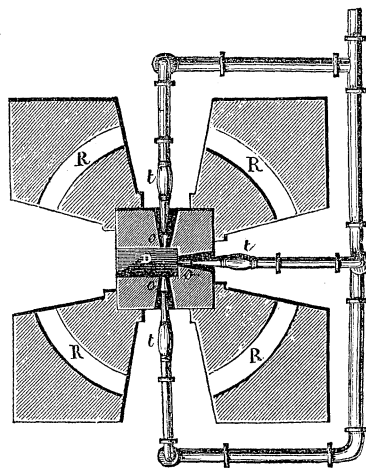


Fig. 485.



on the sides or top of the hill, a bridge *aa'* communicating between this terrace and the platform *pp'* of the mouth. The terrace is reached by an inclined plane, to which the ore and fuel are conveyed by machinery. The material is then transported in wagons on a railway to the platform *pp'*.

The twyers of blast-furnaces are double conical tubes *abcd* of cast-iron, or copper (fig. 486), and as their ends might melt, in consequence of the high temperature to which they are exposed, a current of cold water is continually circulated through them,

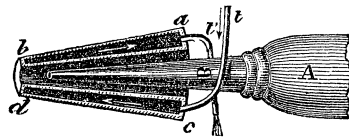


Fig. 486.

which, being introduced through the small tube *t*, runs off through the tube *t'*. The openings of the twyers advance as far as the inner wall of the hearth. The nozzle of the wind-tube *B* is disposed in the twyer, and communicates with the

cast-iron tubes of the blowing-machine by a flexible leather tube *A*. The three twyers are on the same horizontal plane, but the axes of the two twyers on the sides of the hearth are not prolongations of each other, being separated by some centimetres, so that the two currents of air may not interfere with each other.

§ 811. The blowing-machine of a blast-furnace consists of a large cast-iron cylinder *A* (fig. 487), in which works a cast-iron piston

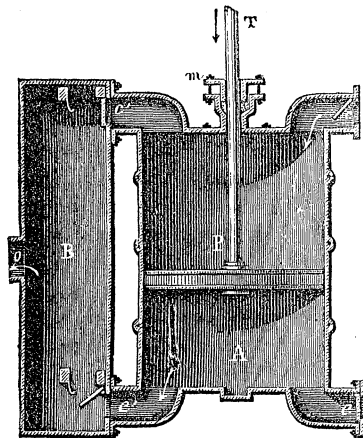


Fig. 487.

*P*, packed with tow or leather to render it air-tight. The cylinder is closed above and below, and on the upper lid is a stuffing-box *m*, through which the piston passes. The lid has also two side-openings *c, c'*, one of which *c* communicates with the external air and is furnished with a valve which opens from without inward, while the other *c'* communicates with a lateral cast-iron cylinder *B* and has a valve opening from within outward. The bottom of the cylinder has also two openings; one at *e*, having a valve which opens from without inward, establishing a communication between the lower

part of the cylinder and the external air; and one at *e'*, which communicates with the lateral cylinder *B*, opening from within outward.

Let us suppose that the piston has reached its maximum ascent, and begins to descend. If the valves *c, c'* are closed, the air will be expanded in the upper part of the pump, and its elastic force will

be more and more feeble; when, the external exceeding the internal pressure, the valve  $c'$  will be forcibly applied against the opening  $c'$  and intercept the communication between the upper part of the pump and the lateral cylinder B. The valve  $c$ , on the contrary, will open, and the external air will enter the upper part of the pump, while the air contained in the lower part will, on the other hand, be compressed into a smaller and smaller space as the piston descends; its elastic force will be superior to that of the external air, the valve  $e$  will be pressed against the opening  $e$ , the valve  $e'$  will open, and the internal air will be driven into the lateral cylinder B, and thence through the opening  $o$ , into the cast-iron pipes which convey it into the twyers. Thus, during the descent of the piston, the external air is inspired by the upper part of the pump, while that of the lower part is sent to the twyers, the inverse taking place during the ascent of the piston, when the lower part aspires the external air, and the upper part sends its air to the twyers. The blowing-machine therefore sends a continual stream of air to the furnace during both motions of the piston, the blast being, however, sensibly weakened at the moment the piston changes the direction of its movement, that is, at the *dead-points* of the alternate movement; and as it is important that the blast should be as regular as possible, a large reservoir is interposed between the cylinder B and the twyers, so as to prevent the variations from being felt in the latter.

The working of the blowing-machine exerts great influence over the blast-furnace; and it is important that the steam engine which moves it should be able to impart greater force than is usually required during the regular working of the furnace, in order that more air may be sent to the twyers when the furnace begins to slacken. A manometer or gauge fitted to the regulating reservoir enables the workmen to judge of the quantity of air sent to the furnace.

In large establishments several blast-furnaces are often fed by the same blowing-machine.

§ 812. The construction of the blast-furnace being well understood, let us now study the process of smelting. We will suppose that the furnace has been just built, or but recently repaired; so that the first process is then to *get up the fire*. It is begun by drying the whole furnace very slowly, as the sudden application of heat would crack the mason-work, and endanger its stability. The anterior part of the hearth is open and the dam-stone  $d$  not yet fixed. In the hearth and the arched space preceding it, fagots are placed to which fire is applied; and while the belly of the blast-furnace acts as a chimney, the inner lining first dries, and then gradually the main body. The fire is kept up for several days, until all danger of cracking the walls by the application of greater heat is over; after which the dam-stone is fixed, and fuel

thrown in at the mouth until it reaches the height of the boshes. When the desiccation is still more advanced, the belly is filled with fuel intended for smelting the ore, and some air is admitted, the blast being gradually increased; and when the fuel has sunk low enough in the belly, a small charge of ore, uniformly spread over the charcoal or coke, is introduced. After some time, more fuel is added, and above it another layer of ore, which process is gradually continued, several days being required to introduce the charge which will be retained during the smelting.

The fuel being the great point of expense in the metallurgy of iron, economy of this article, that is, to smelt the greatest quantity of ore with the same quantity of fuel, has long been the subject of experiment. The proportion of ore is increased as long as the furnace works well and the iron is of good quality; but the charge of ore must be reduced when it fuses with difficulty and furnishes inferior cast-iron.

§ 813. The ore can rarely be smelted without the addition of a foreign substance. Its ordinary gangue is quartz or clay; and now, as in the blast-furnace the gangue and the metal must be reduced to perfect fluidity, in order that they may separate in the hearth by their respective gravity, and as, moreover, it is purposed completely to extract the iron; if the gangue of the mineral is quartz, this substance, being infusible at the temperature of the blast-furnace, can only melt if one or several bases are added to it, so as to form a silicate fusible at this temperature. If a foreign base be not added, the quartz combines with a portion of the oxide of iron of the ore, which it thus preserves from reduction, and forms a fusible slag; in which case a considerable proportion of the iron is lost. But a proper quantity of carbonate of lime will, when added to the ore, pass into the belly of the furnace in the state of caustic lime, which combining with the silicate of alumina, will form a fusible double silicate of alumina and lime, containing base sufficient to prevent it from combining with the oxide of iron, and preventing its reduction. When the ore only contains quartz, both clay and carbonate of lime must be added; but, as the argillaceous ores are much more common than those in quartzose gangues, the latter are always mixed with the argillaceous ores, so that carbonate of lime alone is needed. The carbonate of lime intended for this purpose is in France called *castine*.

In some foundries, where ores of which the gangue is calcareous are smelted, silicate of alumina must be added to obtain a proper slag. In general, argillaceous ores which introduce a sufficient quantity of silicate of alumina are mixed with the calcareous ores. Forge scoriæ, formed of a silicate of the protoxide of iron, very rich in iron, are often added.

The fusibility of the double silicates of alumina and lime varies

with the proportions of their constituent principles. Experiment has shown the most fusible compound of the kind to be that in which the oxygen of the silicic acid is double the oxygen contained in the two bases united. The ratio between the two bases is, moreover, not a matter of indifference; the most fusible compound being obtained by adding to native clay, the composition of which varies but little,  $\frac{2}{3}$  of its weight of carbonate of lime.

§ 814. The fuel used in blast-furnaces is charcoal or coke. Charcoal produces but little ashes, which, moreover, are easily fusible, and introduce no element which can injuriously affect the qualities of the cast-iron. It is sought, in charcoal furnaces, to obtain a slag as fusible as possible, and as free as may be from any considerable quantity of oxide of iron. The composition of this slag therefore resembles closely that of a most fusible double silicate of alumina and lime, that is, of one in which the oxygen of the silicic acid is double of the oxygen of the bases. Coke, on the contrary, gives a considerable proportion of ashes, and sometimes contains a large quantity of pyrites yielding sulphide of iron, which dissolves in the cast-iron and injures its quality. If it is now still sought to obtain the most fusible double silicate of alumina and lime, a large quantity of sulphur will enter into the cast-iron, which greatly deteriorates its quality. Experiment has proved that, in order to avoid this inconvenience, the proportion of the flux must be greatly increased, and a slag must be obtained in which the oxygen of the silicic acid is only equal to that of the united bases. The lime then prevents the greater portion of the sulphur of the pyrites from passing into the cast-iron, and sulphide of calcium is formed, which remains in the slag. But, the slag of coke furnaces being much less fusible than that of charcoal furnaces, it is evident that, in order to obtain a slag sufficiently fusible, the temperature of the coke furnaces must be much higher.

§ 815. The dimensions of blast-furnaces vary, according as charcoal or coke is the fuel used. Charcoal furnaces are generally 30 feet in height, from the bottom of the hearth to the tunnel-head, and commonly have only two tuyers on the sides. Coke furnaces are from 45 to 54 feet high, the capacity of their belly is much larger than that of the charcoal furnace, and they are fed with air by three tuyers.\* The blowing machine impels the air with three or four times as much force as that used for charcoal furnaces. The height of a column of mercury balancing the

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\* In England, from six to ten tuyers are usually employed, and in the former case are sometimes disposed round the furnace in five arched openings, the sixth being introduced through the tympan-stone, a foot or two higher than the others, so that six jets of air, intersecting each other at angles of 60°, are introduced: when ten tuyers are used, one penetrates the front, while the rest are disposed as in fig. 485, each arched opening containing three instead of one.—*W. L. F.*

pressure of the air in the pipes which convey it to the twyers, is, in general, as follows :

In a furnace fed

By very light pine-wood.....	0.8 to 1.2 inches, or	2 to 3 centim.
“ good quality pine-wood...1.2 “	1.6 “ “	3 “ 4 “
“ hard charcoal.....1.6 “	2.4 “ “	4 “ 6 “
“ easily-burning coke.....3.1 “	5.0 “ “	8 “ 13 “
“ hard and compact coke...5.0 “	9.0 “ “	13 “ 19 “

The whole quantity of air projected depends on this pressure and the diameter of the nozzle. Large charcoal blast-furnaces receive at least 1080 cubic feet (40 cubic metres) of air per minute. Coke furnaces never receive less than 1620 cubic feet, (60 cubic metres,) and frequently as much as 2160 or 2700.

§ 816. Let us now examine a blast-furnace in its regular work (fig. 488), and study the various chemical reactions and physical

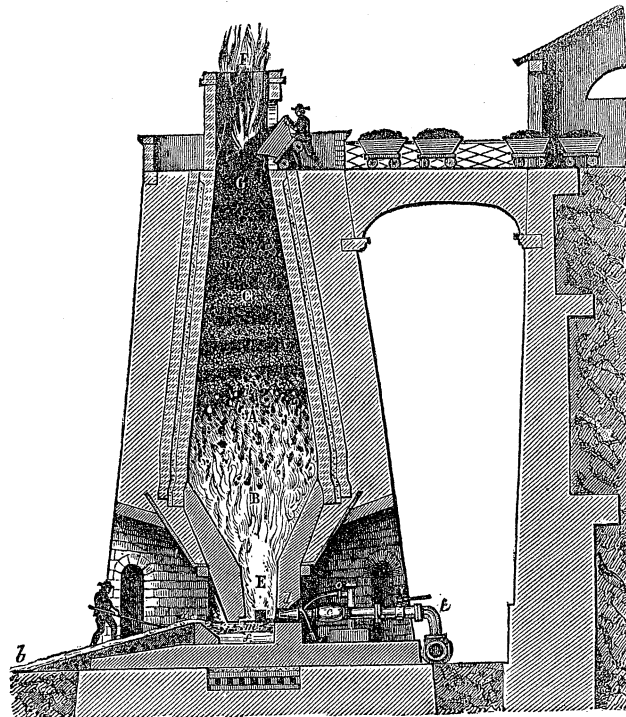


Fig. 488.

phenomena which take place in this vast apparatus. We have said that the ore and fuel are charged, layer by layer, through the mouth G of the furnace: the charges descend regularly toward

the belly A. The temperature is not very high in the upper part of the throat, but is greater in the boshes B; and lastly, in the hearth at E, a little above the twyers, it has reached its maximum. The air, impelled through the twyers, meets with the incandescent fuel, when the combustion is very powerful on account of the excess of oxygen. The charcoal burns to carbonic acid, and evolves all the heat it is capable of yielding by combustion with oxygen. The combustion by oxygen often continues even in the lower part of the boshes, but is much less lively there, because the greater part of the oxygen of the air is already converted into carbonic acid. The gas reaching the middle of the boshes, which is composed of nitrogen and carbonic acid, attains a very high temperature, and imparts a portion of its heat to the fuel and the ore filling the furnace. Now, we have seen (§ 256) that when carbonic acid gas is passed over burning charcoal, the former combines with a quantity of carbon equal to that which it already contains, and is changed into oxide of carbon, which occupies a volume double of that of carbonic acid. But this inverse combustion of the carbon, followed by a great expansion of the gaseous product, far from evolving heat, absorbs it to a remarkable degree: the temperature, therefore, instead of rising, falls, in the lower part of the belly, much below what it would be if the gaseous current, highly heated by the combustion taking place in the hearth, merely shared its heat with the materials it met with. The temperature, which in the boshes is of a reddish white, only reaches a red-heat in the lower part of the belly. The gas in the upper part of the boshes, being composed of nitrogen and oxide of carbon, there meets with the fuel and the ores heated to a dull red-heat; and as, at this temperature, carbonic oxide gas readily decomposes oxide of iron, the latter is entirely reduced, and there results a mixture of gangue and very finely divided metallic iron. The reduction of the oxide of iron regenerates a portion of the carbonic acid, and the flux itself evolves its carbonic acid, by changing into quicklime, so that the gas issuing from the tunnel-head consists of nitrogen and a mixture of carbonic acid and oxide. There is, moreover, a small quantity of hydrogen and carburetted hydrogen, evolved by the fuel, which is always imperfectly carbonized, and of which the carbonization is completed in the belly of the furnace. A certain quantity of hydrogen and oxide of carbon is also formed at the expense of the watery vapour existing in the air impelled by the twyers, and which is decomposed in the boshes by the burning charcoal. The gas leaves the mouth in a very cold state, but is highly inflammable, on account of the great quantity of oxide of carbon which it contains.

§ 817. Thus, while examining only the ascending column of gas which traverses the blast-furnace, we see that the gas is eminently oxidizing in the hearth, where the combustion is most active, and

VOL. II.—G

where the highest temperature prevails. It is often more oxidizing in the lower part of the boshes, but much less than in the hearth, because the greater part of its oxygen is already converted into carbonic acid: the temperature is also much lower, for the combustion is less active. Toward the middle of the boshes, the gas no longer contains oxygen, the carbonic acid being converted into carbonic oxide by contact with the burning charcoal; and as this transformation takes place with absorption of heat, the temperature falls rapidly in this part of the furnace. Above the boshes, the gas is reducing, because it is composed only of nitrogen and oxide of carbon; and, as the temperature is still that of a red-heat, the oxide of carbon reacts on the oxide of iron in the ore throughout the whole of the lower part of the belly, reducing it to metallic iron. But the temperature is not sufficiently elevated to separate the iron from the gangue. As both by the reduction of the ore and the calcination of the flux, carbonic acid is disengaged, the gas issuing from the mouth must contain a considerable quantity of this gas, the temperature of which, however, is greatly lowered, from its having passed through the upper layers of recently introduced fuel and ore, and there cooled, not only because they have abstracted from it heat necessary to elevate their own temperature, but also because a great portion of the heat has become latent, in consequence of the vaporization of the water which moistened the fuel and the ore, or which was in combination with the oxide of iron.

§ 818. Let us now follow the downward march of the ore and the fuel. These substances dry in the upper part of the furnace, and, when they have fallen some metres, reach a temperature at which the hydrated sesquioxide of iron loses its water. A little lower, the reduction of oxide of iron takes place, and the flux begins to lose its carbonic acid; while the reduction of the oxide and the calcination of the flux are completed in the lower part of the belly and the boshes. When the charges reach the bottom of the boshes, where a much higher temperature exists, the lime combines with the gangue of the ore and with the ashes of the expended fuel, forming multiple silicates, which come into fusion at a lower point and constitute the slag. The metallic iron, finding itself at a high temperature in contact with charcoal, in an atmosphere very slightly oxidizing, combines with a certain quantity of carbon, and passes into the state of cast-iron. A small quantity of silicic acid is also reduced by the contact of the charcoal and iron, if the temperature be very high, as it is in coke furnaces; and its silicium combines with the metal. The substances, thus prepared, enter the boshes of the furnace with the balance of the fuel. Combustion there is very active, and the cast-iron and silicates, becoming very fluid, fall by drops into the hearth. But as the air in the latter part is very oxidizing, they must fall rapidly, as otherwise a considerable portion of the iron would again be oxidized and combined

with the dross. It is therefore very important that the belly should be contracted, in order that the substances may soon pass through it. The cast-iron and slag, falling indiscriminately into the hearth, separate according to their densities, the cast-iron occupying the lower part *f* of the hearth, and leaving the slag above. Very soon, the layer of slag reaches the upper level *d* of the dam-stone, and flows over it, when the current of slag thus occasioned is directed over the inclined plane *bd*, and removed, as fast as it becomes solid on the floor of the foundry. The volume of slag is at least 5 or 6 times greater than that of the cast-iron, and the hearth is not entirely filled with the latter until after the lapse of 12 or 24 hours. It is essential to keep a layer of slag over the cast-iron, to prevent the latter from being oxidized by the air from the twyers.

The next step is to tap it. The workmen have made a series of small lateral canals, or rills, in sand, on the floor of the foundry, connecting with a longitudinal canal, which communicates with a hole in the damstone, called the *tap-hole*. The tap-hole, which is made in the hearth, near one of the lateral edges of the damstone, is closed during the smelting with a stopper of clay. In order to draw off the melted iron, the workman removes the stopper with a bar, when the liquid cast-iron runs into all the rills; and when it begins to solidify, he throws a little sand upon it to retard its cooling. During the tapping, the blast through the twyers is arrested, and the blowing-machine is set at work again only when the tap-hole is closed and the hearth empty. The cast-iron is thus run into semi-cylindrical pieces, called *pigs*, or *pig-metal*.

§ 819. Large objects, such as water-pipes, pillars, and parts of steam-engines, etc., are sometimes cast immediately from the blast-furnace. The cast-iron is then run into moulds of sand, constructed in ditches in the floor of the foundry, at a short distance from the furnace, small canals connecting the moulds with the canal which leads the cast metal from the tap-hole. When the moulds are filled, the surplus is run into pigs.

A great number of smaller objects, such as pots, plates, grates, etc., are moulded in the same way. It is, in that case, not necessary to wait until the hearth is filled, but the process can be carried on without interruption during the smelting. The foundry building must be large, as the moulds occupy a considerable amount of space.



Fig. 489.

after the metal has run out, by a clay stopper fastened to the end of an iron rod, so that it can be removed at will.

§ 820. The fused metal of charcoal furnaces can be almost always used immediately for casting, when the ores are not too impure,

The fused metal is received at the tap-hole in sheet-iron vessels (fig. 489) lined with clay, and carried by two men; and the tap-hole is closed,



which is not the case when coke furnaces are used; metal for casting being obtained in the latter only by directing the smelting in a peculiar way, and using a coke which does not contain too much pyrites. We have seen (§ 800) that there are three species of cast-iron—white, gray, and mottled iron; but of these the gray and mottled iron only are fit for casting; white iron being too brittle for ordinary purposes. When gray iron is to be obtained, the proportion of the ore must be less than the maximum power of the charcoal, as otherwise the least derangement in the working of the furnace would produce white cast-iron.

The working of the blast-furnace may be ascertained by the flame at the tunnel-head, by that at the tymplate, the appearance of the twyer, that of the cast-iron, the regularity of the descent of the charges, and principally by the nature of the slag. The workmen thus can know when it may be necessary to increase or diminish the charge of ore.

§ 821. The relative dimensions of the various parts of the blast-furnace greatly influence its working. Now, several of these parts, principally the belly and boshes, become, after a time, altered by the corroding action of the slag and the high temperature to which they are subjected; and when the furnace then works to a disadvantage, it is often necessary to modify the relative proportions of the fuel and ore, to introduce more charcoal, and even to stop and *blow out the furnace*, when the cast-metal can no longer be obtained of sufficiently good quality.

At the beginning of the smelting, the belly is narrow, and the materials descend into it slowly. If the fuel falls in sufficient quantity, the materials remain long enough in the region of the highest temperature for the cast-iron and slag to acquire the fluidity necessary for the perfect separation of these substances in the crucible part; but if the charcoal burns easily, as it does when made from light wood, and if, moreover, the blast be strong, then but little charcoal will reach the belly, the oxidizing space will rise very high in the boshes, the reduced iron will not remain long enough in contact with the charcoal to combine with the quantity of carbon necessary to convert it into an easily fusible cast-iron, and a portion of the iron will be oxidized by passing through the air of the twyers, and pass into the slag. The crucible will therefore contain only a half-refined cast-iron, not sufficiently fluid, and the yield of the furnace will be small, because a considerable quantity of the iron will be lost in the slag. Frequently, also, masses of non-carburetted iron, which, consequently, are difficult of fusion, adhere to the sides of the boshes immediately above the twyers, where they are cooled by the blast, and obstruct the draught.

If, on the contrary, the belly is too large, and not sufficiently high; if, moreover, the charcoal burns with difficulty, or the blast is too feeble, then the combustion will be very active in the belly imme-

diately above the twyers, but the temperature will be too low in the boshes. The materials will not be sufficiently prepared on their arrival in the boshes, not having had time to attain the proper temperature; the slag will be doughy, and the furnace may become choked.

An inconvenience of the same nature occurs when ore in compact rocks, impervious to gases, or forge-cinders are smelted. The oxide of iron is reduced with great difficulty by the carbonic oxide gas in the upper parts of the furnace, because the reducing gas cannot penetrate the small masses of metal; the reduction is therefore effected by the charcoal alone and in the belly itself, when the fused materials flow on the fuel. The materials do not remain long enough in contact with the charcoal to effect the perfect reduction and separation of the cast-iron. The ore is then said to be difficult to melt, to be *refractory*; but it would be incorrect to say that it is difficult to reduce. This inconvenience is lessened, in the case of the compact ores, by subjecting them to a preliminary roasting, which disaggregates and renders them porous.

Generally speaking, the working of a blast-furnace must be stopped when its belly and boshes become too much enlarged by the corroding action of the slag. As it would then be necessary greatly to increase the quantity of fuel, it is more profitable to stop and repair the furnace. A well-constructed furnace should continue in blast for at least 2 years; but, under favourable circumstances, some furnaces have lasted for 4, 5, and even 6 years. When the furnace is out of service, it is emptied completely, allowed to cool, and the interior torn out, while the main body rarely requires any repairs, and need not be touched.

§ 822. The cold air impelled into the blast-furnace absorbs a considerable portion of the heat developed by the combustion in the boshes, in order to attain the temperature which there exists. This absorption of heat is diminished, and, consequently, all other things being equal, the temperature rises higher in the boshes if, instead of using cold air, an equal weight of air previously heated to  $400^{\circ}$  or  $600^{\circ}$  is impelled. The materials which are difficult of fusion, and do not become sufficiently fluid in a cold-blast furnace, melt perfectly when it is fed by hot air, while such charcoal as is of difficult combustion burns more easily, because the combustibility of charcoal is in proportion to the elevation of temperature. The most refractory materials may, therefore, be fused with hot air, and dense fuel may be used which would burn with difficulty in a cold-blast furnace.

When a hot-blast furnace is set at work with the ore and fuel adequate for a good smelting in a cold-blast furnace, the proportion of the fuel may be considerably diminished, and a good blast yet be obtained; but it is important to remark that the substitution of heated for cold air remarkably modifies the reactions which

take place in the various parts of the apparatus. The quantity of charcoal is smaller, and, moreover, it burns more rapidly; and, therefore, the quantity of air introduced being in proportion to the charcoal burned, the weight of gas which traverses the furnace during the rotation of the hot air is less in comparison with the weight of the ores. Now, as the temperature of the boshes is supposed to be the same in both cases, there will be, in the middle and upper part of the furnace, less heat with the hot blast than with the cold, and the charcoal being more combustible, the space of the maximum of temperature will be more confined. These two causes determine important modifications in the nature of the chemical reactions which take place in the various parts of the furnace, particularly in front of the twyers, and they may exert a considerable influence on the quality of the cast-iron obtained.

The economy of fuel effected in the blast-furnace by the use of hot air, would lose a great deal of its importance if it were necessary to burn charcoal to heat the air; and the combustible gases which issue from the tunnel-head are therefore applied to this purpose. To effect this, an oven is built above the mouth or immediately at its side, surmounted by a chimney, in which cast-iron pipes, traversed by the air of the blowing-machines, are inserted. The flame of the tunnel-head enters this oven, and if the pipes are properly arranged, the air may be heated to  $500^{\circ}$  or  $600^{\circ}$ .

In the majority of foundries in which hot air has been substituted for cold, there is considerable economy of fuel effected, while unforeseen difficulties have also arisen, causing this new application to be abandoned, so that only few hot-blast furnaces are now in use. The working of the furnace was more difficult, and the quality of iron yielded very irregular.

§ 823. The combustible gases which escape from the blast-furnace are capable of producing by burning a quantity of heat greater than that developed in the blast-furnace itself, and not one-half of the heat evolved by the fuel in this apparatus has yet been advantageously applied.

In fact, experiment has proved that 1 litre of vapour of carbon produces, by its complete combustion, 2 litres of carbonic acid, and evolves 7858 units of heat; that is, a quantity of heat capable of raising the temperature of 7858 times its weight of water by one degree (*Celsius*). Two litres of oxide of carbon, containing 1 litre of vapour of carbon, consume 1 litre of oxygen, and yield, by burning, 2 volumes of carbonic acid and 6260 units of heat. The quantity of heat evolved by the transformation of 1 litre of vapour of carbon into 2 litres of oxide of carbon is therefore only 1598 units, or 0.234 of the total quantity of heat which the same quantity of carbon evolves by complete combustion and conversion into carbonic acid. It may be easily concluded thence that carbonic acid, by being converted into oxide of carbon, absorbs a

considerable quantity of heat; and thus is explained the cooling which takes place in the blast-furnace above the boshes. In fact,  $\frac{1}{2}$  litre of vapour of carbon yields, by complete combustion, 1 litre of carbonic acid, and disengages 3929 units of heat, while 1 litre of carbonic acid combines with  $\frac{1}{2}$  litre of vapour of carbon, yielding 2 litres of oxide of carbon, which, by complete combustion and transformation into 2 litres of carbonic acid, evolve 6260 units of heat. Thus, in these successive combustions, 1 litre of vapour of carbon has yielded a sum total of heat disengaged equal to  $3929 + 6260 = 10189$ . The same litre of vapour of carbon, burning completely immediately and being converted into carbonic acid, would disengage 7858 units of heat. The conversion of 1 litre of carbonic acid into 2 litres of carbonic oxide, therefore absorbs a quantity of heat represented by  $10189 - 7858 = 2331$  units, which are again evolved when the oxide of carbon burns in order to be transformed into carbonic acid.

The heat disengaged by a  $\frac{1}{2}$  litre of vapour of carbon burning in the belly of the furnace, and being converted into carbonic acid, is represented by 3929 units. In the boshes, the carbonic acid formed combines with a  $\frac{1}{2}$  litre of vapour of carbon, and causes 2331 units to pass into the latent state. If the very feeble calorific effects which are produced during the reduction of the ores by the combustible gases be neglected, there is no other evolution of heat in the blast-furnace, and combustible gases therefore burn at a dead loss, or escape from the tunnel-head of the furnace, by disengaging 6260 units of heat, which is a quantity of heat nearly double of that used in the blast-furnace itself.

In latter years, attempts have been made profitably to use this great loss of heat. We have said that it had been used to heat the air projected into the blast-furnace; but it has been also employed for the preliminary roasting of the ore, and is now applied to heating the boilers of the steam-engine which drive the blowing-machines, as the gases from the mouth of the furnace evolve, while burning, a quantity of heat sufficient to give the necessary motive-power. Still further progress has been made in some foundries: the gases from the blast-furnace have been drawn out at the distance of several metres below the mouth, and carried by pipes into reverberatory furnaces, where they were burned with a proper quantity of air, by which means a temperature was obtained in these furnaces sufficiently elevated to perform many metallurgic operations, especially the transformation of cast into bar iron.\*

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\* This is a mistake; for although experiments have been made, simultaneously, in different parts of Southern Germany, in Hungary, Bohemia, and in France, and, at a later period, also in the United States, to employ the lost heat of blast-furnaces for puddling, etc., they were all a signal failure, having been made in works where charcoal was employed as fuel, which, developing a more limited quantity

§ 824. The cast-iron used for moulding immediately as it leaves the furnace is generally the fine-grained, gray cast-iron, as free as possible from graphitous particles, which would make the iron porous. Frequently objects of cast-iron are made, the surface of which should be very hard; as for example, certain cylinders used in rolling. A thick cast-iron mould is used, into which the fused metal is poured, generally through the lower part of the mould. The metal, suddenly cooled by the contact of the thick mould, which is a good conductor of heat, passes into the state of white cast-iron in the neighbourhood of the mould, and its surface becomes very hard, while the interior of the cylinder remains in the state of gray cast-iron, and retains malleability sufficient to prevent the piece from breaking.

§ 825. A large portion of cast-iron is used in foundries remote from the furnaces in which it is made. These foundries are generally situated in large cities or their environs, so as to be able to cast at short notice the objects ordered. Sometimes, very large pieces are required, demanding more metal than can be contained in the hearth of a single furnace; and, in such cases, the mould-

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of combustible gases than bituminous coal, could not afford sufficient heat for the purpose; and besides, as fast as the cast-iron was purified by the process of puddling, fresh impurities were constantly being brought in with the gases. Another great difficulty was that of obtaining a constant temperature. The remarks in the text probably refer to a patent, taken by Sire, in 1838, in France, which, to the best of my knowledge, never was worked, and consisted in drawing off the blast-furnace gases at the boshes, and burning them in reverberatories immediately adjacent; a process by which the working of the blast-furnace must necessarily be greatly impaired.

The method now almost universally employed to make use of the waste heat, is the invention of M. Faber du Faur, of Wurtemberg, consisting of drawing off the gases a short distance below the tunnel-head of the furnace, and burning them, partly in chambers, in which the pipes conveying the blast are arranged, by which the air is heated to 600° or 800°, and partly under the steam-boilers of the blast-machine, with jets of air.

Experience has shown that combustible gases cannot, without affecting the process in the blast-furnace, be drawn off at more than one-sixth of the whole height of the furnace below the tunnel-head. The best process is, however, decidedly that employed in several furnaces in England since 1851, especially at Ebbw-Vale; in which case, a truncated inverted cone is inserted in the tunnel-head, while the under opening is entirely closed by another cone, placed upright, and held in its place by a chain, lever, and counterpoise. The charge is thrown into the funnel thus formed, and sinks into the furnace by lowering the under cone: the advantage of spreading the charge perfectly equally in the furnace is thus gained, and *all* the waste gases are drawn off by flues set above the level of the charges. The working of the furnace is not in the least impaired by having the mouth closed.

The gases escaping from furnaces where certain kinds of bituminous coal are employed, contain a percentage of ammonia, which may be obtained by leading the gases through a solution of dilute chlorohydric acid, or chloride of calcium, which is cheaper: a solution of sal-ammoniac is thus obtained after some time, from which the salt may be gained by evaporation and sublimation. If the gases are to be burned after the washing, they will, moreover, have lost their carbonic acid, which has entered into combination with the lime of the chloride of calcium, and will thus be greatly improved in quality.—*W. L. F.*

ing is done after a second fusion. For small objects, as those made of Berlin iron, the cast-iron is again melted in large earthen crucibles, heated in a forge-fire or blast-furnace, while, for larger objects, reverberatories or *cupola-furnaces* are employed.

The cupola consists of a furnace A made of fire-bricks (fig. 490), from 9 to 12 feet high, and bound together by cast-iron plates. The fire-bricks do not extend as far as the outer casing of iron, but are separated from it by a layer of sand or broken forge-cinders. The furnace is built on mason-work, covered by a large cast-iron plate *ef*, which serves as a base for the furnace and its

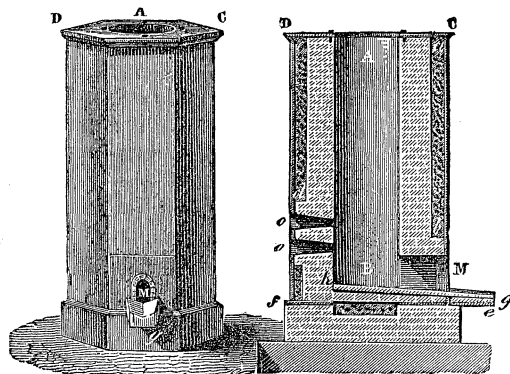


Fig. 490.

iron case; while the upper end of the furnace is covered by a plate of cast-iron DC, holding the outer case together, and provided with an aperture corresponding to the mouth. Two or three layers of fire-bricks are laid on the plate *ef*, and upon them clay is heaped, so as to form a plane *hg*, slightly inclined toward the

tap-hole *g*, so that it acts like the floor of a hearth for the fused metal.

The cupola-furnace is fed by a blowing-machine, which impels the air through two twyers, placed sometimes above each other, as in the furnace represented in fig. 490, and sometimes near each other in the same horizontal plane.

The bottom of the furnace being first filled with charcoal and lighted wood, coke is thrown on, the air-blast admitted, and when the combustion is in active operation, the fuel and cast-iron are added in successive layers. The fused metal collects at the bottom of the furnace, and the smelting must be effected as rapidly as possible, in order that the cast-iron may not be changed in quality in passing before the twyer. When the cupola contains a sufficient quantity of fluid iron, it is tapped; and if large objects are to be cast, the moulds are arranged near the furnace, the melted metal being run into them by rills communicating with the tap-hole. Sometimes, three or four cupola-furnaces are required to furnish the amount of fluid metal necessary. When small objects are to be cast, the fused iron is received in vessels like that represented in fig. 489, and carried to the moulds in the different parts of the foundry.

As reverberatory furnaces permit the remelting of a larger quantity of iron than cupola-furnaces, and consume less fuel, they are preferred for casting large pieces; but in the former the cast-iron is subject to more alteration than in the cupola-furnaces, because it meets with a more oxidizing air, which deprives it of a portion of its carbon. It is essential that the air entering these furnaces should pass through a grate, so as to possess as feeble an oxidizing power as possible. Lastly, the fusion must be made rapidly; for which reason the cast-iron is placed on the floor of the hearth only when the furnace is in full blast.

All kinds of cast-iron cannot be moulded after a second fusion: they must be rich in carbon, so as to be able to lose a small quantity of it, without becoming too difficult of fusion.

#### OF THE CONVERSION OF CAST-IRON INTO BAR-IRON.

§ 826. In order to convert cast-iron into bar-iron, the carbon and silicium combined with it must be removed, which is effected by subjecting it to an oxidizing action, which changes the carbon into carbonic acid and the silicium into silicic acid, which latter, combining with the bases, principally with the oxide of iron, forms fusible silicates, which separate in the form of slag. When the cast-iron contains small quantities of sulphur and phosphorus, which is sometimes the case, these must also be separated during the refinery, as they injure the quality of bar-iron, and may even render it unfit for use. This separation is very difficult, and occasions considerable waste; the presence of these two metalloids in cast-iron is therefore avoided as much as possible. If sulphur exists in the ores, it is separated almost completely by previous roasting; but if it is furnished by the fuel, as happens when coke made from pit-coal is used, a large quantity of flux is required in the blast-furnace, in order that the slag may retain the sulphur in the state of sulphide of calcium. Cast-iron containing any considerable quantity of sulphur or phosphorus always yields iron of an inferior quality.

When a blast-furnace only produces iron intended for refining, the smelting is generally so conducted that a white cast-iron, containing but little carbon, is obtained, which is effected by introducing a great deal of ore, and forcing the air so as to cause a rapid descent of the materials; but this can only be done with very pure ores and fuel, as otherwise an impure cast-iron, yielding iron of inferior quality, would be obtained.

If cast-iron be kept, at a high temperature, in contact with the air, its surface becomes covered with oxide of iron, which reacts on the inner layer of the iron: the carbon of the cast-iron reduces the oxide of iron, and is disengaged in the state of carbonic oxide gas, while the silicium effects a similar reduction and produces silicic

acid, which, combining with a portion of the undecomposed oxide of iron, forms a fusible silicate, the composition of which varies according to the proportion of oxide of iron which enters into it; but generally it assumes the formula  $3\text{FeO}, \text{SiO}_3$ . If, in fact, a more basic silicate, such as  $6\text{FeO}, \text{SiO}_3$ , be heated in contact with cast-iron, a portion of the oxide of iron is reduced by the carbon of the cast-iron, and the silicate has a tendency to assume the composition  $3\text{FeO}, \text{SiO}_3$ . Cast-iron reacts even on this latter silicate, but less readily and at a higher temperature; so that the silicates which have a tendency to form resemble closely the formula  $3\text{FeO}, \text{SiO}_3$ . The conversion of cast into bar iron is founded on this reaction. The silex of the scoriæ is furnished not only by the silicium of the cast-iron, or the grains of sand adhering to its surface, and which come from the moulds in which it has been cast, but a great portion is also produced by the ashes of the fuel used for the refinery.

Two different processes are used for refining cast-iron:

1. Refinery with charcoal, called *refinery in the small furnace*.
2. Refinery with pit-coal, called *refinery by the English method*, or refinery by *puddling*.

*Refinery by the small furnace.*

§ 827. The refinery is effected in a small quadrangular furnace U (figs. 491 and 492), made of iron plates, covered with clay, the depth of which is 9 inches, its width varying from  $1\frac{1}{2}$  to 2 feet. The air is conveyed by a twyer *t*, which enters the furnace to the distance of about 4 inches, in such a direction that its prolonged axis would cut the opposite face of the hearth at its lower edge. The copper, or baked-clay twyer, which is represented in fig. 493, generally receives the nozzles of two wooden bellows S, S' (figs. 491 and 492), moved by a water-wheel. The bellows are arranged so as to afford a continuous blast; and while the movable frame of the one descends and impels the air into the furnace, the other ascends and inspires the external air; the quantity of air being regulated by the flow of water on the wheel. The blowing-machine we have figured is very imperfect; and double cylindrical machines, resembling that in fig. 487, the blast of which is regulated by a register in the air-pipe, are substituted for it in modern forges.

In the front of the furnace is a cast-iron plate *aba'b'*, placed at the height of the upper opening of the furnace, and slightly inclined. At the lower part of the hearth is a tap-hole, which opens at the bottom of the hearth, and serves for the escape of the scoriæ. The furnace is covered by a basket-funnel C, having a chimney which carries off the gases arising from the combustion, and sheet-iron plates P are fastened to the funnel, to protect the workmen from the heat.



Fig. 491.

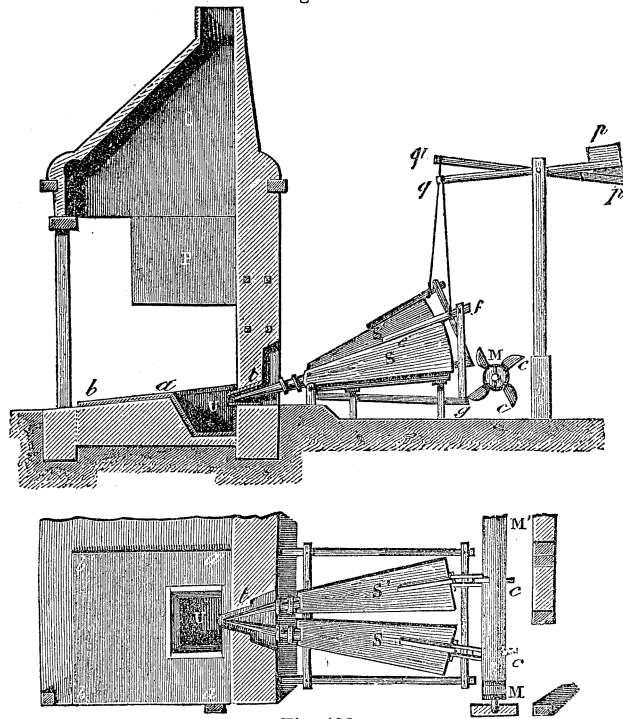


Fig. 492.

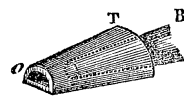


Fig. 493.

The furnace, while containing the charcoal kindled in a preceding operation, is filled with fresh charcoal and the air admitted. The cast-iron to be refined is either in the form of pigs or plates, and, when melted, drops to the bottom of the hearth, passing the air of the twyer. The smelting lasts from 3 to 3½ hours. The workmen take advantage of the high temperature developed by the combustion of the charcoal which is placed above the cast-iron, to forge bars of refined iron arising from the preceding operation, as we shall presently explain. The surface of the drops of cast-iron, passing through the air of the twyer, becomes oxidized, and a very basic silicate of iron is formed, which reacts on the carbon of the cast-iron, so that the latter, when it has arrived at the bottom of the hearth, has lost a great portion of its carbon, and becomes much less fusible. From time to time, the scoriæ are withdrawn by opening the tap-hole, a sufficient quantity to continue the decarbonizing action always being left. Frequently the workman allows the air of the twyer to blow directly on the cast-iron, to increase its oxidation.

When the mass of iron, partly refined, has become consistent, the workman raises it with his bar above the fuel, which he heaps at the bottom of the furnace, when the air then blowing below the mass subjects it to a powerful oxidizing action. Fresh charcoal is added and the force of the blast increased, so as to fuse the metal a second time. After the second fusion, the refining is very far advanced; and the iron forms spongy masses, which the workman collects together and welds into one single piece; while he sometimes draws those pieces which do not appear sufficiently refined nearer to the twyer. When the operation is terminated, the scoriæ are completely removed, the mass of iron is withdrawn, its sides are beaten with iron bars, and it is then carried to the hammer.

The hearth is then cleansed. A portion of the scoriæ is left in the furnace, and the remainder withdrawn, but generally preserved for use in the following operation during the smelting of the iron, for which the scraps of iron detached during the forging of the lump are also made use of. When the iron plate forming the bottom of the hearth becomes too hot, it is cooled by a small quantity of water.

§ 828. The process to which the lump is subjected when it leaves the furnace, consists in placing it on an anvil, when it is beaten in all directions by a heavy hammer (fig. 494). The anvil E is gene-

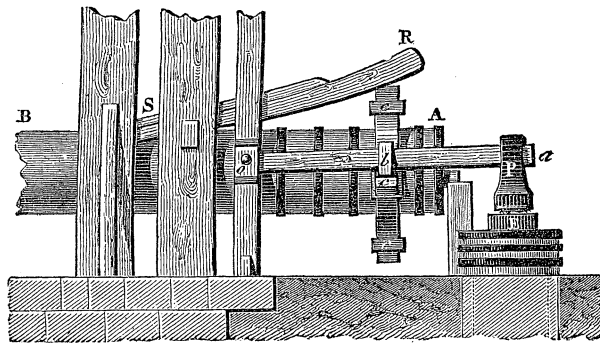


Fig. 494.

rally of cast-iron, while the hammer is frequently made of wrought-iron, with a steel face. The head P of the hammer weighs from 600 to 1200 pounds, and is mounted on a wooden helve from AB, strengthened by bands of iron. The helve is held in a cast-iron ring, provided with two gudgeons o, on which it revolves, and which rest on cast-iron collars fastened to uprights. To give additional solidity to the anvil, it is placed on a large block of wood, resting on pile-work driven into the floor of the foundry. The hammer is raised by cams c, c, averaged on an anvil AB, which is turned by a water-wheel, and, when it is elevated to b,

VOL. II.—H

strikes against a piece of wood SR, called a *rabat*, or check, which prevents it from rising too high; while the check also, by virtue of its elasticity, imparts to it a rapid descending motion, which prevents it from meeting the following cam before striking on the anvil. The *flight* of the hammer, or its greatest separation from the anvil, varies from  $1\frac{1}{2}$  to 2 feet. The hammer first described, is called a *forge-hammer* (*marteau à soulèvement*).

§ 829. In order to carry the glowing bloom to the anvil, the workmen use strong iron tongs, during which operation the hammer is held in the air by means of a chock. As soon as it is completed, the chock is removed and the water-wheel set in motion, at first slowly, the rapidity being gradually increased, when the very fluid scoriæ scattered through the spongy metal are expressed by the compression and run out, while the metallic particles are welded to each other. The workmen turn the bloom on its various faces, in order to strike it in all directions; when it takes the form of an elongated prism, with a square base, which is cut into 4 or 5 pieces, called *lopins*, with an iron knife, the back of which is exposed to the hammer. When the furnace has been arranged for a new smelting, the *lopins* are introduced into it, covered with charcoal, and, when they have attained a sufficient temperature, are forged into bars.

§ 830. The forge-hammer is sometimes used for this purpose, but most generally a smaller hammer, called a *tilt-hammer*, is employed. This hammer, represented in fig. 495, which gives a greater

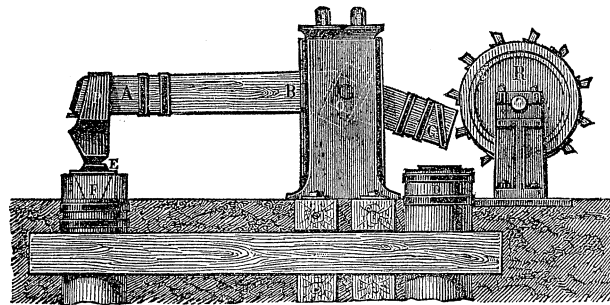


Fig. 495.

number of blows, and does not rise so high, is moved by its heel, by means of cams on the shaft R of the water-wheel. The axis of rotation O is placed at  $\frac{1}{3}$  of the length of the helve, starting from the heel C; and the cams bear from above downward on the heel of the helve, and, in this way, elevate it. They are much more numerous around the circumference of the shaft than those of the forge-hammer. In order that the hammer may fall quickly, after the cam has passed, its heel is made to strike against a piece of iron, fixed in a block of wood D, which actively repels it, and allows

the hammer to fall back on the anvil before being raised by the succeeding cam.

Refinery in the small furnace yields 72 to 76 parts of bar-iron from 100 of cast; the iron always being of very good quality when the cast-iron is not very impure, because the metal has been forged and beaten in every way. Good quality iron may also be obtained from very moderate quality cast-iron; but the loss is, in that case, much greater.

§ 831. Hot air is also used for the refinery of cast-iron in the small furnace; the air, before reaching the twyer, being conducted through a series of pipes arranged in a serpentine form above the furnace, and in the chimney surmounting it. It has been ascertained that it is only necessary to use hot air during the first stage of the process, that is, during the smelting of the cast-iron, because it then was effected more rapidly; and to throw in cold air during the second stage, when the oxidation should be more active. But the use of hot air during the operation of refining has been abandoned in the majority of foundries which at first adopted it, because the working is more irregular than with cold air.

It has been endeavoured to substitute coke for charcoal in refinery by the small furnaces, but the quality of the iron was always indifferent.

*Refinery by pit-coal, or the English method.*

§ 832. In all countries where wood is scarce, and mineral fuel, on the contrary, plentiful and cheap, a process of refinery very different from that just described is adopted, called *refinery by the English method*, because it originated in England. This operation is divisible into two consecutive parts, which are executed in different furnaces.

In the first operation, the cast-iron is fused in a kind of refining crucible, in contact with charcoal and exposed to the air of the twyer, when the melted metal runs into a large rill, where it assumes the shape of a plate. By this fusion under the twyer, the cast-iron has lost a portion of its carbon and nearly all its silicium, and forms a white, short, and brittle metal, more or less blistered, and called *fine-metal*. The furnace in which this fusion is executed is called a *running-out fire*.

The refinery of fine-metal is completed by exposing it in a reverberatory furnace, at the same moment, to a very high temperature and to a current of oxidizing air, when the carbon of the cast-iron burns to carbonic acid, while, at the same time, the iron oxidizes on its surface, and yields magnetic iron, which, partly combining with the silicic acid produced by the silicium yet contained in the fine-metal, forms a kind of slag, which covers the small fragments of metal arising from the disaggregation effected by heat. The oxide of iron in the scorixæ, reacting on the carbon which still

remains in combination, disengages carbonic oxide, which burns with a small bluish flame, while sometimes scoriæ rich in oxide of iron are added to hasten the combustion. When the workman thinks the refinery is completed, he collects the fragments of metallic iron scattered over the floor of the reverberatory furnace into the shape of balls, which he removes in succession, carrying them to the shingling hammer to be worked into bars. This second operation finishes the refinery, and is called *puddling*: the iron is called *puddled iron*.

Refinery by the English method corresponds to the first fusion of the cast-iron under the air of the twyer in refinery by the small furnace. The fine-metal presents nearly the same composition as the fused metal which collects at the bottom of the small furnace after the first smelting.

§ 833. The running-out fire is composed of a rectangular crucible A (figs. 496 and 497), made of cast-iron boxes U, through

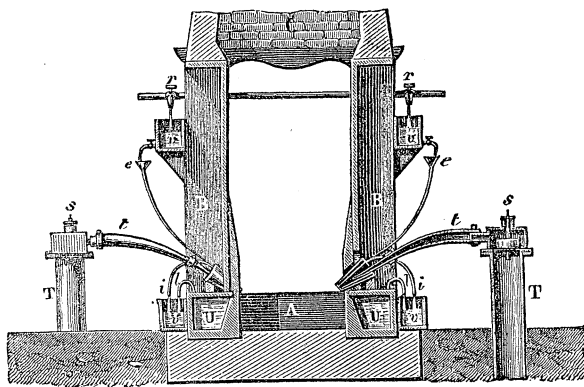


Fig. 496.

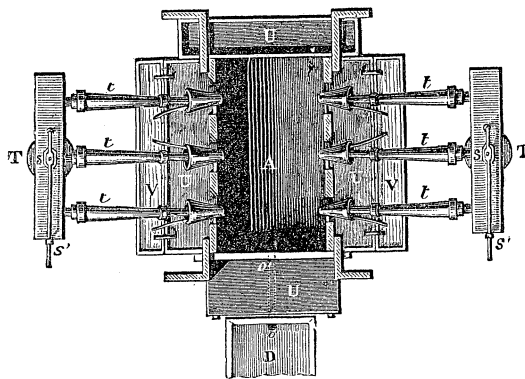


Fig. 497.

which a current of cold water circulates continually to prevent them from melting. The bottom of the crucible is made of sand; and the blast is furnished by 6 twyers, disposed on the two sides. The twyers are of cast-iron, double, and resembling those (fig. 486) used in blast-furnaces. Cold water, coming from the boxes *v*, and regulated by stopcocks *r*, circulates constantly in the twyers to prevent their fusing at the high temperature of the furnace. A cylindrical blowing-machine, worked by a steam-engine, furnishes the air necessary, which, impelled by the machine, first enters a cylindrical reservoir *T*, whence it is distributed through the pipes *t*, furnished with nozzles fitting the twyers. The reservoir *T* has a register *s*, by means of which the quantity of air projected into the furnace can be regulated. The twyers are so inclined that their prolonged axes would cut the opposite vertical faces of the crucible, at a little distance from their lower edge. The furnace is surmounted by a chimney *C* to carry off the gaseous products of the combustion, supported by a cast-iron frame *B* having several apertures, through which the men can work in the crucible. The front part of the crucible is furnished with a tap-hole *oo'*, for the escape of the melted metal, which flows, with the scorixæ, into an oblong iron trough *D*, for sudden congelation.

§ 834. The operation of the running-out fire is continuous. After the metal has run out, the workmen clean the crucible, remove the scorixæ, introduce the burning charcoal, cover it with the proper quantity of coke, and heap upon it iron pigs, which are about 3 feet in length, and weigh from 90 to 120 pounds. The pigs are arranged symmetrically over the surface of the furnace: the charge generally consists of from 20 to 24 cwt. Sometimes the cast-iron is gradually introduced. When the furnace is charged, the blast is let on, feebly at first, when the iron melts and drops through the air of the twyers, where the portion of it which is oxidized forms a slag with the ashes of the fuel and the silicic acid arising from the oxidation of the silicium of the cast-iron; the slag, which is very rich in oxide of iron, again exerting a decarbonizing influence on the cast-iron which it covers. The workman judges of the progress of the refining by the appearance and consistence of the fluid metal; when the latter has entirely fallen into the crucible, the air of the twyers is allowed to blow for some time over the surface of the liquid bath, and then the man proceeds to open the tap-hole, when the metal flows into the large trough *D*, where it spreads in a sheet-like form, and the scorixæ flow over it. When the crucible is empty, water is thrown on the fine-metal to congeal it rapidly and render it very brittle. If the metal still retains some sulphur, a very decided smell of sulphuretted hydrogen is evolved. The scorixæ are removed and the fine-metal broken with a hammer. The colour of the fracture of this metal is of a grayish-white, the upper layers being filled with blisters, while the lower ones are

compact. During this operation, the cast-iron has lost all its silicium, but only a portion of its carbon.

An idea of the chemical change which cast-iron undergoes by refining, may be formed from the following analyses:—A cast-iron composed as follows,

Carbon.....	3.0
Silicium.....	4.5
Phosphorus.....	0.2
Iron.....	92.3
	<hr/>
	100.0

yielded a fine metal composed of

Carbon.....	1.7
Silicium.....	0.5
Iron.....	97.8
	<hr/>
	100.0

Cast-iron loses, in the running-out fire, about 10 per cent. of its weight, the consumption of coke being about 16 cubic feet for every ton of fine-metal obtained.

§ 835. The puddling-furnace is a reverberatory furnace of which fig. 499 represents a horizontal, and fig. 498 a vertical section, while fig. 500 gives a perspective view. The floor of the furnace is perfectly horizontal; but posteriorly, at B, there is a depression

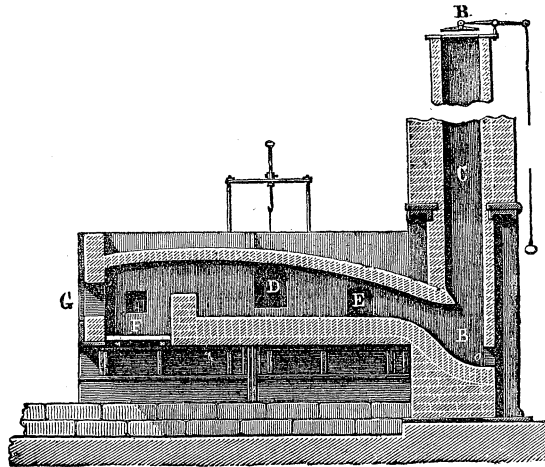


Fig. 498.

leading to an opening *o*, through which the scoriæ are withdrawn, and which remains shut during the operation. The floor is separated from the grate *F* by a fire-bridge of about 9 inches in height, while the draught is effected by a brick stack *C*, from 30 to 45 feet high,

and furnished with a register R, which the workman can regulate from the foundry by means of a chain. The walls of the reverberatory furnace are built

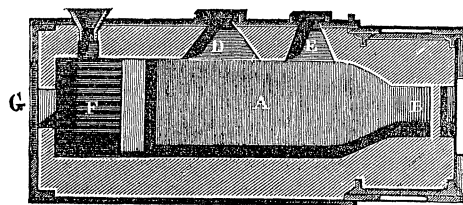


Fig. 499.

of refractory bricks, and covered externally by iron plates, held in place by iron tie-rods. The furnace has several doors; those F and G communicating with the grates, and serving for charging the fuel, are closed by registers. The doors D and E communicate with the floor of the furnace; D is chiefly used during the refinery, and can be closed by a register; E is closed

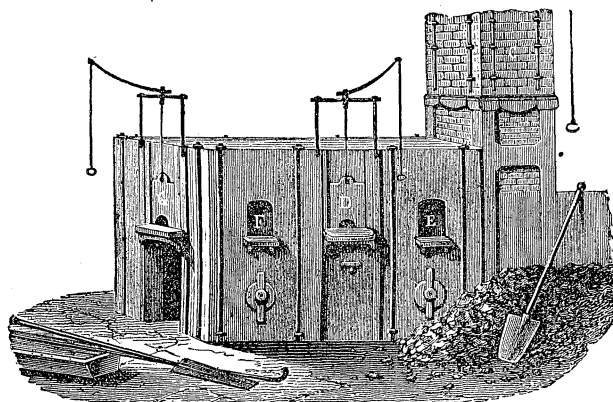


Fig. 500.

during the operation, and is used only for cleaning the floor and charging the metal to be refined. The floor is often made of a simple iron plate, under which the air circulates freely, to prevent it from becoming hot enough to fuse. At other times it is covered by a layer of sand; while, lastly, in some foundries, the floor is made of fire-bricks covered by a bed of scoriæ heated nearly to a fusion.

The grate of an ordinary puddling-furnace is square; and about 3 to  $3\frac{1}{4}$  feet deep. The floor is 5 to 6 feet in length,  $3\frac{1}{2}$  feet in its greatest width toward the grate, and  $1\frac{1}{2}$  feet near the chimney.

§ 836. The following is a description of the operations in puddling. The furnace being heated to a white red-heat, from 4 to 5 cwt. of metal are introduced and spread over the floor, while about 1 cwt. of rich scoriæ or scraps of iron are added; after which the doors are closed hermetically, and the register in the chimney opened. As soon as the metal fuses, the register R in the chimney



is gradually lowered to diminish the draught. The half-melted metal is covered with liquid scoriæ, and the workman stirs it continually with a bar, which he passes through the door D—opening this door to as small an extent as possible, so as not to allow the introduction of too much fresh air in the furnace, lest the iron should become too completely oxidized. He then opens the register R, when the carbon of the cast-iron reacting on the oxide of iron of the scoriæ, causes a great quantity of carbonic oxide gas to be evolved, which, escaping through the scoriæ, causes them to boil up and swells the whole mass. The gas burns with a small blue flame. The workman continues to stir the mass with his bar, until he recognises, by the appearance and pulverulent consistence of the metal, that the refining is sufficiently advanced; after which he allows a portion of the scoriæ to run off, and collects the portions of refined iron together with the bar, welding them to each other by pressure. When he has thus formed a metallic ball, he rolls it over the floor of the furnace covered with red-hot fragments of iron, which adhere to the ball, which, when it has attained a sufficient size, he pushes toward the bridge, and immediately begins to make a second. In this way he makes 4 or 6 balls, which are carried successively to the hammer, beginning with the one first made.

Fourteen or sixteen charges are generally made in 24 hours; the loss of the fine-metal being about 7 or 8 per cent., while about 100 parts of pit-coal are consumed for 100 parts of puddled iron.

The previous refining of the cast-iron is indispensable in very siliceous metal produced in coke blast-furnaces fed with impure ores or a fuel containing a large quantity of pyrites. When the metal to be refined is very pure, as that produced in charcoal furnaces, or the very pure gray cast-iron yielded by certain coke furnaces, the previous run-out fire is often omitted, and the iron is puddled immediately. In this case, the operation occupies rather a longer time, and occasions a greater loss.

§ 837. The hammer with which the blooms from the puddling-furnace are wrought is represented in fig. 501, and consists entirely of cast-iron, weighing from 3 to 6 tons. The axis *o* of the helve

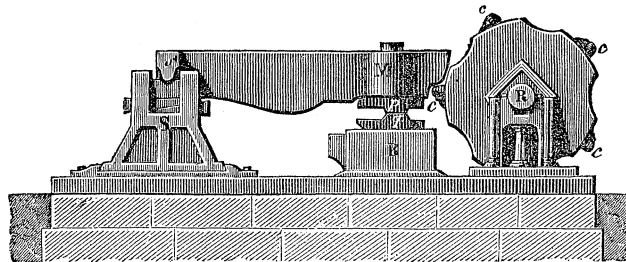
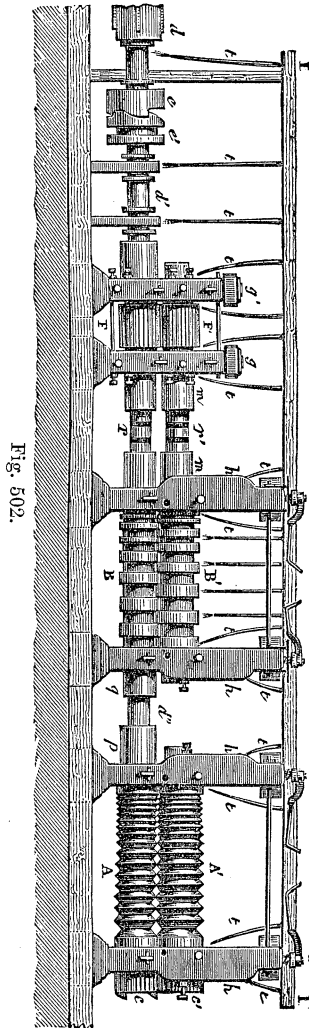


Fig. 501.

turns in collars let into the cast-iron support S : the pane or head *p* is of steely iron, and composed of three parts fastened by wedges into the cast-iron helve. The wood-cut represents the usual shape of the pane of the hammer and the anvil *q*. The hammer is raised by its head, by means of cams *c, c* mounted on a ring of cast-iron, called the *cam-ring bag*, which is itself fastened to a horizontal shaft R, moved by a water-wheel or steam-engine. The flight of this hammer varies from  $1\frac{1}{2}$  to  $2\frac{1}{2}$  feet, the number of blows being about 75 to 100 per minute.

§ 838. The *roughing-rolls* (fig. 502) are composed of two horizontal cylinders, placed upon each other, having their surfaces grooved in various ways, according to the shape to be given to the bars. The axes of the two cylinders must be exactly in the same vertical plane, and they are driven by equal forces, but in opposite directions, the lower roller receiving its motion directly from the machine on the axis of which it is fixed, while the upper cylinder is moved by the first, by means of the gearing *c, c'*, and, consequently, revolves in an opposite direction. The cylinders, being set in cast-iron frames, *h, h*, rest on brass chains, and their separation is regulated by a screw *a*. The cylinders A and B are connected with each other and with the rotating axis of the machine, by cast-iron collars *m*, which pass over both axes and are fastened with keys; the cylinders are thus readily taken apart and put together again. The cylinders A, A' are furnished with square grooves, which decrease regularly from the first to the last, and are intended for the manufacture of square bar-iron. The cylinders B, B', on the contrary, are arranged for the production of flat bar-iron.

In order to prevent the cylinders from becoming too much heated during the process, small streams of water, furnished by the tubes *t, t, t*,



communicating with the pipe I I', are allowed to fall on them.

In order to introduce the heated bars, the workmen hold them with pincers, and rest them on a plate of sheet or cast iron, called an *apron*, placed on a level with the line of separation of the two cylinders; while a second plate, the edge of which is notched so as to allow the grooves of the lower cylinder to pass, is arranged on the other side of the cylinders at the same height, and is intended to receive the bar on its exit, and prevent it from wrapping around the lower cylinder. When the bar has passed out, a workman seizes it with his tongs, passes it above the upper cylinder, where the roller receives and present it to a second groove, of which the section is smaller. The operation is facilitated by resting the bar on hooks suspended to chains, the ends of which slide along horizontal bars. The puddling-rolls generally make 30 or 40 revolutions per minute.

§ 839. After this short description of the machinery for rolling iron, let us return to the process of puddling. The puddled bloom, withdrawn from the fire, is dragged along the floor of the foundry to the anvil, on which it is placed by means of strong tongs, called a *porter*. The hammer is raised as high as possible by a wedge, and, in order to set it in motion, the cam-ring bag is made to revolve, while a bar of iron is applied to one of the cams, exactly as it passes near the face of the hammer. The hammer is then raised, the wedge removed, and the former goes on working. The scoriæ scattered through the spongy metal flow out copiously, while the metallic particles are welded to each other, and the bloom being hammered in various directions, assumes the shape of an elongated prism with a square base. The hammering does not last more than a minute, so that the bloom is still very hot, and may be sent immediately to the rollers. When the iron has successively passed through the several grooves of the roughing-rolls and the rollers, it has assumed the shape of flat bars of about half an inch in thickness and 2 or  $2\frac{1}{2}$  inches in breadth.

§ 840. Recently, a hinge-press (fig. 503) has been substituted for the hammer above described for compressing the blooms from the puddling-furnace, consisting of two cast-iron jaws AB and D

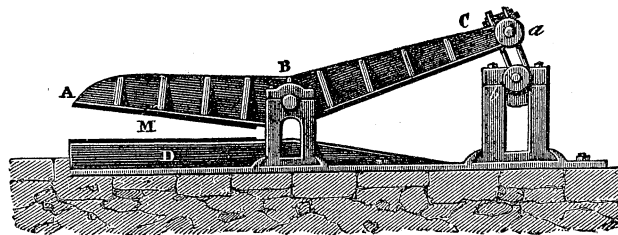


Fig. 503.

joined together like a pair of scissors; but, instead of cutting edges, they have plane surfaces, slightly grooved, between which the spongy iron is forcibly compressed. The lower jaw D is made of a cast-iron box through which water can circulate, while the upper jaw is moved by an iron crank *ab*, mounted on a shaft *b* set in motion by a machine. The press occasions less loss than the hammer, and enables the bloom to pass sooner through the rollers.

§ 841. Lastly, a new apparatus has been invented,\* which presents great advantages even over the press, for the forging of the bloom, and the working, in general, of large masses of iron: the *stamping-hammer* or *steam-hammer*. The hammer (fig. 504) is

composed of a cast-iron stamper C, weighing from 3 to 5 tons, and terminating below in a steely-iron pane A, to which any desired shape is given. The stamper moves in iron grooves *ab*, *cd*, fixed in a solid cast-iron frame, and is supported by an iron rod *tt*, attached to a piston which moves in a pump P, erected on the upper platform of the frame: the anvil B being immovably fixed at the bottom of the same frame. In order to raise the stamper, high-pressure steam is introduced into the trunk of the pump P, below the piston, which, rising in the pump, carries the stamper with it. If the communication be-

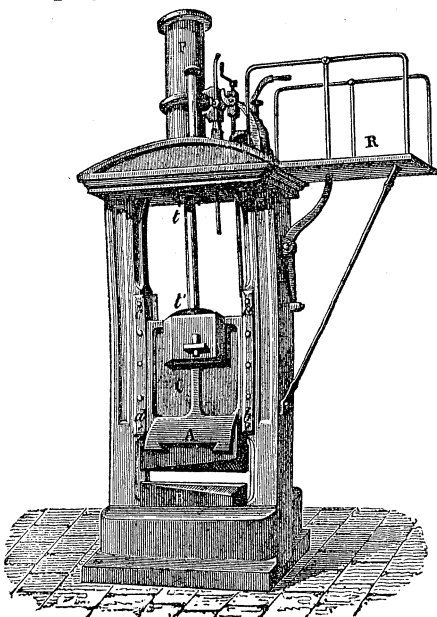


Fig. 504.

between the pump P and the boiler be cut off, and, on the contrary, a communication established with the atmosphere, the steam escapes, the excess of pressure which caused the stamper to ascend is removed, and it falls with its whole weight on the anvil. This operation is easily effected by slide-valves such as are used in a steam-engine. A workman, standing on the platform R, works the valves by hand and regulates at will the play of the hammer. The rapidity and number of the blows may be thus regulated, and the hammer can be arrested at any distance from the anvil, which last condition is very valuable, because an exact size can be given to

\* Invented by Mr. Nesmith, of Patricroft, near Manchester, England.—*W. L. F.*

the pieces forged. The steam-hammer is of immense importance in iron-works, particularly for the forging of large pieces, such as the shafts of the wheels of large steam-vessels.

§ 842. Puddled iron is always of inferior quality, being badly welded and filled with cracks or *flaws*; but it generally possesses great hardness, and is well adapted to certain uses in which a better quality of iron is unnecessary. The rails of rail-roads are always made of puddled iron; the bars intended for their manufacture being passed through rollers, the grooves of which are so arranged as to give them the shape generally adopted for rails, a section of which is seen in fig. 505.



Fig. 505.

§ 843. The quality of puddled iron is greatly improved by reheating it to a white welding-heat and again hammering and rolling it. To do this, the bars of puddled iron are cut into lengths of about 8 inches, by means of shears (fig. 506) composed

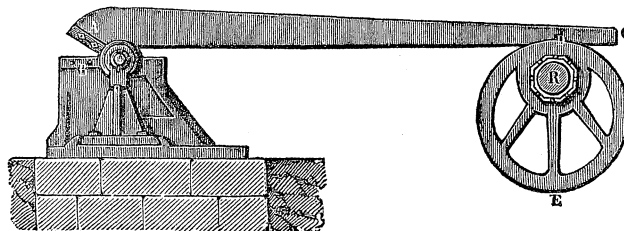


Fig. 506.

of two jaws terminating in steel cutting-edges A, B. The lower jaw B is fixed, while the upper jaw A turns around a horizontal shaft fastened to the lower jaw, and ends in a long iron heel AC, moved by an eccentric wheel DE, of which the axis of rotation R is turned by water or steam power.

The divided ends of the puddled iron are placed upon each other, so as to form bundles, each of which contains the quantity of iron necessary to make a bar; and the bundles are introduced into a reverberatory, called a *reheating furnace*, and represented in figs. 507 and 508. This furnace differs from the puddling-furnace, in having a larger capacity A and a greater surface of grate F: it has only two doors, one for charging the fuel, while the other *o*, at the back part of the furnace, immediately below the chimney, serves for the introduction of the bundles of iron to be reheated, and for their removal when completed. This door is closed by a register *r*. It is important to admit only air entirely deprived of its oxygen into the furnace, in order to prevent the iron from oxidizing and occasioning considerable loss; for which reason the doors of the furnace must be kept as closely shut as possible, so that no air shall enter but that which has passed over the grate. As the working-door is immediately below the chimney, the exter-

Fig. 507.

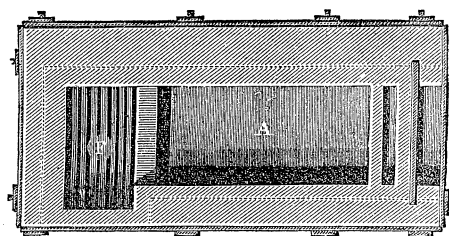
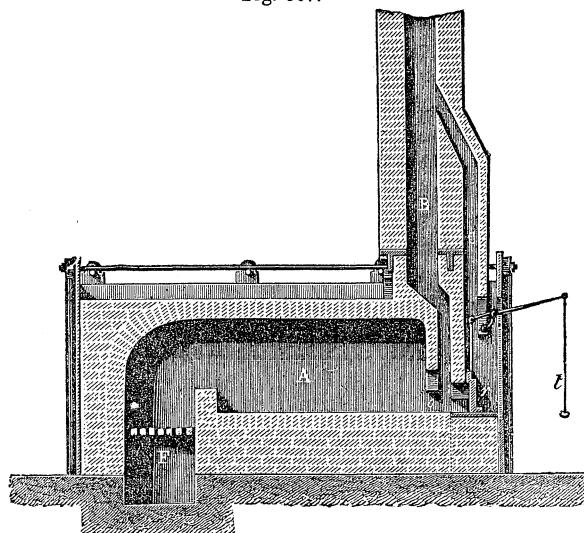


Fig. 508.

nal air does not enter the furnace when it is opened to remove a bundle, but goes directly up the chimney. When the bundles have attained the temperature of a white welding-heat, they are successively removed, and passed between the extension-rollers, which are much more carefully made than those for the puddled iron; being exactly turned, so as to give clean surfaces and sharp edges to the bars. They also revolve more rapidly, especially for objects of small size, as it is important in this case that the bars should pass rapidly, in order that they may retain sufficient heat until the dimensions required are attained.

§ 844. In order to accelerate the process of rolling small objects, three grooved cylinders, placed one above the other, are generally used, the middle one of which is moved by the machinery, and turns the others in opposite directions by suitable gearing. The bar is first passed between the first and second cylinders, when the workman on the other side receives it, and immediately passes

it between the second and third cylinders, the rollers making from 150 to 200 revolutions per minute.

§ 845. In latter years it has been attempted to use the gases escaping from the mouth of the blast-furnace as fuel for puddling cast-iron. The gases were drawn off by pipes placed a few metres below the tunnel-head, and conveyed into the puddling-furnace, the chimney of which was sufficient, when the furnace was in blast, to produce the proper degree of draught. The combustible gases, the current of which was regulated at will, were burned with a proper quantity of atmospheric air, and yielded a long flame which extended through the furnace. The temperature thus obtained was sufficient for puddling, but the process was difficult, the loss being often greater than in puddling with pit-coal, and the quality of the iron being irregular; for which reasons, puddling with combustible gases taken from the blast-furnace has been nearly abandoned, despite its great economy of fuel. These gases have been more profitably used in heating the boilers of the steam-engines which furnish the motive-power; but it is then necessary to have at least one auxiliary boiler, which can be heated directly by coal, in case the working of the furnace should be deranged: this is an indispensable precaution when the engine is intended to drive the blowing-machines, the blast of which must be increased, if, by any accident in the blast-furnace, a more considerable volume of air is required.\*

*Manufacture of Sheet-iron and Tin-plate.*

§ 846. Iron rolled out into thin laminæ is called *sheet-iron*. For its manufacture, iron heated to redness is compressed several times successively, either by hammers or rollers—one single operation not being sufficient to reduce the sheet to the degree of thinness required.

The hammer used for the manufacture of sheet-iron resembles the forge-hammer used for forging bar-iron, and weighs about 4 cwt., the dimensions of its plane being about 13 inches by 36. The face of the anvil is slightly convex, and varies in breadth from 2 to 4 inches.

Two sets of cylinders are used for rolling sheet-iron—a roughing and a finishing set, differing merely in the fact of the cylinders of the latter being turned with more accuracy. Fig. 509 represents a set of rolling cylinders. The cylinder A is moved by machinery, and, by means of the cog-wheels F, turns the cylinder A' in an opposite direction; the separation of the cylinders being regulated by the screws  $\alpha$ ,  $\alpha'$  which bind together the pedestals of the upper cylinder.

We shall not stop to describe the process of making sheet-iron by hammering, as it is fast disappearing before the improvements

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\* See the note at page 79.—*W. L. F.*

made in rolling. Hammering produces strong sheet-iron of a good quality, but rarely of uniform thickness.

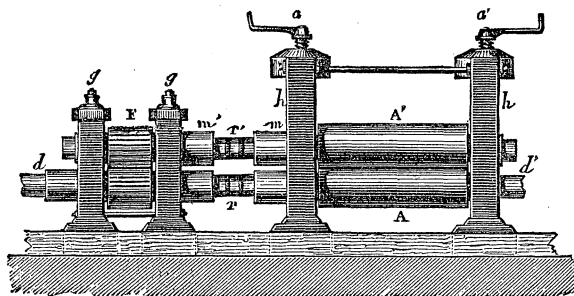


Fig. 509.

The iron used in the manufacture of sheet-iron should be soft and malleable; iron made with charcoal being requisite for thin sheets used in the manufacture of tin-plate, and such thicker plates which are exposed to great resistance, as boiler-iron. The thick plates are made of puddled iron, but they are always of inferior quality, unless the iron has been subjected to several puddlings.

The iron, when wrought into flat bars, of a size proportioned to that of the sheets to be made, is cut with shears into pieces, called *bidons*, equal in length to the intended width of the sheet, while the bars, still hot, are withdrawn from the extension-cylinders. After a quick reheating in a reverberatory furnace, the *bidons* are passed between the rollers, the length of the bar being parallel to the axis of the rollers, and are thus passed 3 or 4 times between the cylinders, which are approximated to each other every time by means of the screws *a, a'* (fig. 509); after which the sheets are heated in a second furnace, from which any air that might oxidize their surface is carefully excluded. The reheated sheets are passed through the finishing-rollers, which give them the thickness and dimensions required, and the plates of sheet-iron obtained are then freed from the adhering oxide, by being hammered with a wooden mallet. When the sheet-iron is required for the manufacture of tin-plate, and consequently must be made very thin, several sheets are laid upon each other, and after being heated to a dull red-heat to anneal them, are compressed between two plates by a hydraulic press, which renders their surface perfectly plane.

§ 847. Sheet-iron, on account of its cheapness and great tenacity, is very extensively used, but the readiness with which it oxidizes in a moist atmosphere would limit its application, were not this inconvenience remedied by the process of tinning, which is described in the following manner.

The sheet-iron is first scraped perfectly clean, by being dipped



for a few moments into dilute sulphuric acid, and then heated to redness in a reverberatory furnace; and it is then passed between highly polished rollers, and allowed to remain for 24 hours in a fermented acid liquid. Being taken out of this liquid, it is plunged for a few moments, first into a dilute solution of sulphuric and chlorohydric acids, then into fresh water, and lastly, it is dried by rubbing it with bran. The sheets are then ready for tinning.

Several rectangular boxes are arranged alongside of each other in the same furnace: a first box A (fig. 510) contains melted grease, in which the sheet-iron is left for  $1\frac{1}{2}$  hour. The workman then dips it into the box B, containing melted tin, where it remains also  $1\frac{1}{2}$  hour. The sheets are then put to drain on an iron grating, after which the workman dips them into a third box C containing impure tin, which detaches the excess of tin remaining on the sheets after their first immersion in the melted metal; after which they are removed and cleaned with a brush. The surface



Fig. 510.

of the sheets then retains only the tin which is incorporated with the iron, by having formed a true alloy. Lastly, the workman plunges them into a fourth box D, containing very pure tin, which covers them with a brilliant coating; and afterward he places them in a fifth box E, containing melted tallow, which causes the surplus of tin to run off and collect in a small ball toward the lower edge of the sheet. It suffices to immerse this edge, for a few moments, in a sixth box F, containing melted tin to a few centimetres in depth, to detach the little ball.

§ 848. The surface of the tin covering sheet-iron is frequently perfectly smooth and brilliant, while its internal texture is crystalline, which can be shown by dissolving the superficial layer by an acid; when the surface of the sheets becomes watered, and often presents a beautiful appearance in reflected light. The acid liquid used for producing this metallic watering is a kind of aqua regia, made of

2 parts of chlorohydric acid,  
1 " of nitric acid,  
3 " of water.

The patches in the watering vary in size according to the slowness of cooling of the tin, the appearance of which can, however, be altered at will. By passing a hot soldering-iron over the reverse of the watered surface, the tin is again melted, but solidifies as soon as the hot iron is removed, thus causing a new crystallization; but as it takes place much more rapidly than the first crystallization, a finer watering results, which forms figures in the original watering. The watered tin-plates should be immediately coated with a transparent varnish, which may be of different colours, to

prevent their tarnishing in the air, which would soon take place without this precaution.\*

*Manufacture of Iron-wire, or Wire-drawing.*

§ 849. Very tenacious and ductile iron alone can be used for the manufacture of wire, unless steel is to be employed. The process of wire-drawing is very simple, consisting merely in passing iron rods through perforations in a steel plate, called a *wire-plate*, which are perfectly round, their diameters decreasing as the wire is extended.

Formerly, thick iron-wire was made by drawing the iron rod, the end of which was seized with a pincers, through the wire-plate, by means of machinery; but it was mashed wherever it had been grasped by the pincers.

In the more modern processes, the iron is first wrought into rods of from  $\frac{1}{4}$  to  $\frac{1}{2}$  inch in diameter, generally by heating square bars of iron, rolled in ordinary rollers and cut into lengths of from  $1\frac{1}{2}$  to 3 feet, to whiteness in a reheating furnace, and then passing them through the rollers described § 844, which revolve about 250 times per minute. The first groove of the cylinders is oval, while the remainder are circular. The iron bar, which passes in less than a minute through 10 of these grooves, and comes out in the shape of a round rod of  $\frac{1}{4}$  to  $\frac{1}{2}$  inch in diameter, is, after cooling, coiled into a circle, and then heated to a dull red-heat in a furnace, to give it all the malleability possible by suitable annealing. It is then rolled on the bobbin FG (fig. 511) of the drawing-bench, the

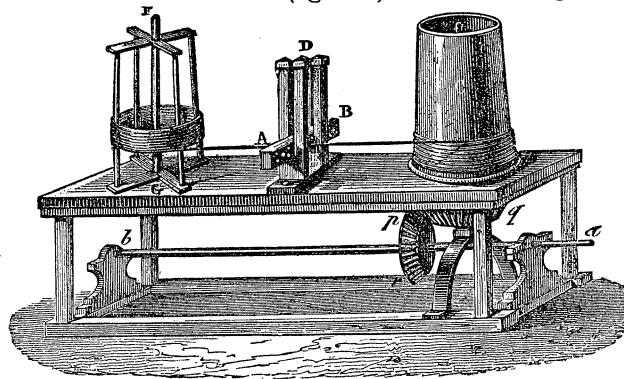


Fig. 511.

free end of the wire being pointed, and passed through the first hole of the wire-plate AB. A second cast-iron bobbin C, slightly conical, is furnished with a small chain and pincers, which seizes the iron-wire as it leaves the wire-plate, and obliges it to wind around

\* The described process of watering tin-plate is called *japanning*.—W. L. F.

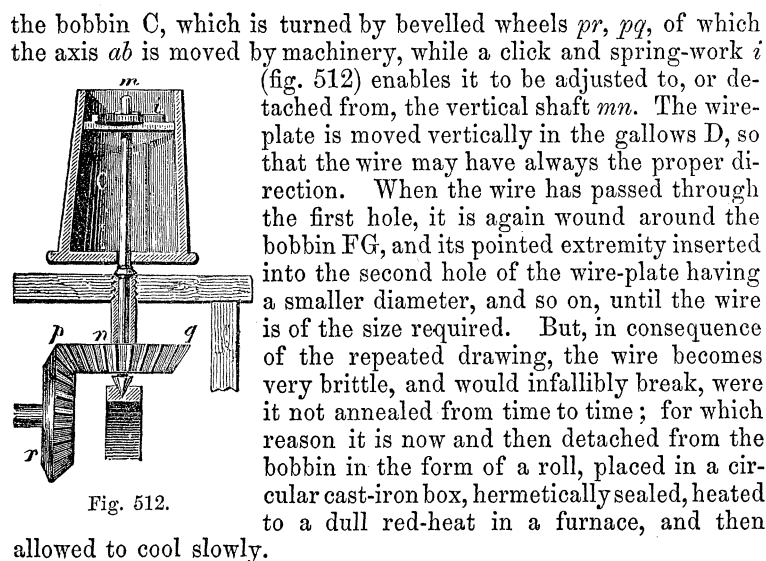


Fig. 512.

allowed to cool slowly.

#### *Manufacture of Steel.*

§ 850. The manufacture of steel may be conducted by two opposite processes: either by partially decarbonizing very pure cast-iron, or by combining wrought-iron with a certain quantity of carbon by the process of *cementation*, that is by heating bars of iron, for a long time, in contact with charcoal. The steel obtained by the partial refining of cast-iron is called *native*, or *forge-steel*, while that prepared by cementation bears the name of *bar* or *blistered steel*. To render both native and bar steel homogeneous, the bars are generally broken into pieces, made into bundles, and heated to a white welding-heat, to be again forged into bars, either by the hammer or the extension-cylinders. These operations are, frequently, repeated several times, and the steel resulting is called *refined steel*, or *shear-steel*; while steel rendered homogeneous by heating it to the fusing point in earthen crucibles bears the name of *cast-steel*, and possesses entirely peculiar properties.

Steel differs from wrought-iron chiefly in the peculiarities it acquires by *tempering*, that is, by suddenly plunging it when hot into cold water, which operation renders it very hard and brittle, while the properties of malleable iron are not sensibly altered by a similar process. The iron which hardens most by tempering is the *steely* kind, and is most esteemed for certain purposes.

§ 851. Steely iron is often endeavoured to be manufactured by the metallurgic treatment of ores according to the Catalan method (§ 808). The workman then lessens the quantity of greillade which he generally adds during the operation, hastens the fusion of the

ore, frequently cleans away the scoriæ, in order to diminish their decarbonizing action on the metal, and keeps the bloom covered with hot coals, to protect it against the action of the current of air. He knows, moreover, by the physical characters of the bloom, when to stop the operation. The blooms are drawn as usual, but the bars, still hot, are plunged into cold water, by which the steely parts become very brittle, and are easily hammered off. Steely iron is chiefly used for agricultural implements, such as ploughshares, scythes, etc.

§ 852. Native, or forge steel, which can be made only from very pure cast-iron, is extensively manufactured in Germany, principally at Siegen,\* in Styria, and in Silesia. The brilliant laminated cast-iron yielded by the manganiferous sparry ores in charcoal furnaces is generally used, and is refined in a small furnace resembling that for the refinery of cast-iron made with charcoal. The hearth being filled with burning coals, 6 or 7 plates of laminated cast-iron, arranged vertically in the furnace, are successively melted in it, under the influence of a strong blast; a certain quantity of rich scoriæ and scraps of iron being added at the commencement of the operation. When the first plate has fallen to the bottom of the hearth the material is at first perfectly liquid, but the oxidizing action of the scoriæ, very soon depriving it of sufficient carbon to destroy its fluidity, renders it doughy. The second plate is then fused, which, falling to the bottom of the hearth, liquefies the whole mass. Under the oxidizing action of the air and the scoriæ, the material again loses its fluidity by parting with a portion of its carbon, and then a third plate is added, and melted in the same manner as the first, but so that the liquid drops shall fall into the centre of the doughy mass at the bottom of the hearth. This time the mass does not liquefy entirely, the central parts alone becoming fluid. The process is continued in this manner until 6 or 7 plates are melted, making a weight of from 3 to 4 cwt.; the scoriæ are then removed, and the bloom is withdrawn and divided into 7 or 8 wedge-shaped pieces, the composition of each of which is similar, while they still are far from being homogeneous in all their parts, as there exists a great difference between the centre and the circumference of the mass. They are hammered out and converted into bars of about 2 inches square, during the fusion of the cast-iron in a second operation, and are plunged, while still hot, into cold water to temper them, and then handed to the refiners. During this incomplete refinery of the cast-iron, the consumption of charcoal is very considerable, and reaches 846 cubic feet of charcoal for every ton of crude steel.

§ 853. Bars of crude steel vary very much in different parts of their length, as one of the ends is always more carburetted than

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\* The steel manufactured at Lohe, near Siegen, is thought to be the best article of the kind: the ore employed is the manganiferous sparry iron of the celebrated iron mountain (Stahlberg) at Muesen.—*W. L. F.*

the other. The refiner, holding the bar by its less carburetted end, strikes it across an anvil, thus causing the harder portion instantly to break off; by striking still harder, he effects the separation of a second portion, less steely than the first, and a bar of steely iron remains in his hand, which he cannot break by a blow, and which he sets aside to be used for sharp agricultural implements. The portions detached by the blow, destined for the manufacture of steel of superior quality, are sorted according to the appearance of their grain, and are rendered more homogeneous by several successive processes of refining. The workman lays a bar of hard steel on one of softer steel, melts the whole at a white welding-heat, and transforms it under the hammer into a flat bar, which he immediately tempers. These flat bars are again broken into pieces and tied in bundles, taking care always to place a hard and soft bar together, by which successive operations the material becomes more and more homogeneous, but the waste and consumption of fuel is rapidly increased. The material also loses more and more of its carbon during the reheatings, and would be converted into pure iron if the bundles were not covered with a coating of pure clay, which, melting by the assistance of a small quantity of oxide of iron, preserves the material from the direct contact of the air.

§ 854. Bar or blistered steel is prepared by heating thin bars of iron for a length of time in contact with charcoal at a high temperature, always, however, below the point of fusion; when the carbon, first combining with the iron of the surface, soon penetrates it and unites successively with the various layers. It is evident that a homogeneous cementation cannot take place throughout the whole thickness of the bars, as the external parts have already become steel while the inside is still in the state of wrought-iron, and are converted into hard steel when the inside has just commenced to become soft steel; and lastly, the former approach the composition of cast-iron when the central portions are hard steel. The cementation of iron is effected in large rectangular boxes C (fig. 513), made of refractory bricks, in an arched oven M, the

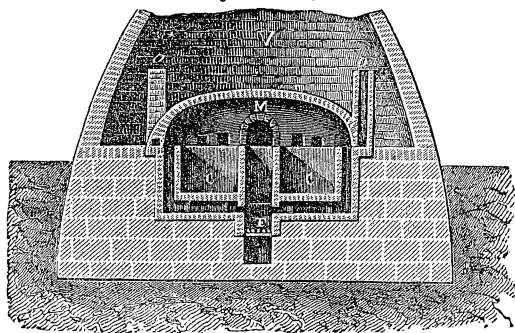


Fig. 513.

hearth of which is at F. The flame and smoke escape through small vent-holes *o, o* into the chimney V. The boxes, resting on small bridges of brick, and surrounded by vacant spaces through which the flame circulates, are from  $7\frac{1}{2}$  to 15 feet in length, from  $2\frac{1}{4}$  to 3 feet in width, and as much in height. Wood or pit-coal is burned on the grate.

The *cement* is made of powdered charcoal, to which  $\frac{1}{10}$  of its weight of ashes and a little sea-salt are frequently added. The part played by these two substances in the process of cementation has not been yet explained. In order to charge a cementation-box, a layer of cement to the depth of about 2 inches is first spread in it, and on this a layer of iron bars is arranged edgewise, so as to leave between them a space of somewhat less than a  $\frac{1}{2}$  inch. The bars are not quite so long as the box, so as to allow room for free expansion: a section of them is a rectangle of about  $1\frac{1}{4}$  to 2 inches by  $\frac{1}{4}$  to  $\frac{1}{2}$  inch. Between and above the bars a layer of cement about  $\frac{1}{2}$  inch in thickness is placed, then a second layer of bars, and so on, until the box is filled to within about 6 inches of the top. It is then closed hermetically with refractory bricks, or better still, with a layer of quartzose sand. The two boxes of a furnace contain from 10 to 20 tons of iron, according to their size.

Each box has several openings corresponding to working-holes in the wall of the furnace, through which some of the bars can occasionally be withdrawn to estimate the progress of the operation by their appearance. The proper temperature, which is nearly that of the fusing point of copper, is attained in 24 hours, and kept up for 7 or 8 days. Cementation advances more rapidly at a higher temperature, but in that case the products are still less homogeneous. When the cementation is supposed to be completed, the furnace is allowed to cool for several days before being emptied, when the surface of the bars is covered with small bubbles, or blisters, from which circumstance the steel has received the name of *blistered steel*. This steel can be used only after having been made more homogeneous by fagoting or by fusion. About 50 lbs. of pit-coal are used for 2 cwt. of crude steel.

Bar-steel is refined nearly in the same way as bar-iron. Bundles, made of several bars, sorted by placing the hard on the softer bars, are heated in small blast-furnaces fed with pit-coal, and then new bars are made of them, either by hammering or rolling, which are tempered and then broken into several pieces. Other bundles are made of the fragments, and they are again forged. The fagoting is repeated once, or several times, according to the quality of steel to be manufactured, as the steel becomes softer at each fagoting by losing a portion of its carbon.

§ 855. Iron or steel articles, when finished, are sometimes subjected to cementation, by an operation called *case-hardening*, in order to harden their surface. The articles, arranged in layers

with cement, in sheet-iron boxes, are heated to a high temperature in boxes surrounded by hot walls, which are renewed until the process is judged to be completed, which is known by pieces of iron-wire, penetrating the boxes and removable at pleasure. The cemented articles are tempered by immersion in cold water. Steel objects, of which the surface has been softened so that they might be more easily wrought, are often case-hardened. In order to soften the surface of a steel object, it is heated in a heap of iron filings, and then allowed to cool slowly.

§ 856. Steel acquires a perfectly homogeneous character only by fusion, and then takes the name of cast-steel. The fusion is effected in fire-clay crucibles, in a common furnace, consisting of a small rectangular chamber A (fig. 514), of 3 feet in depth, and of which a horizontal section is  $1\frac{1}{2}$  by  $1\frac{1}{4}$  feet. The chamber is lined with an infusible quartzose grit, and communicates with the chimney C by a horizontal throat B, the draught being regulated by a register *r* in the chimney. The upper part of the furnace is open, to allow the introduction of the crucible and the fuel, but the opening is covered by a lid made of refractory grit, or fire-bricks held together in an iron frame. Several of these melting-furnaces are generally arranged along-side of each other, while their chimneys are united in the same stack.

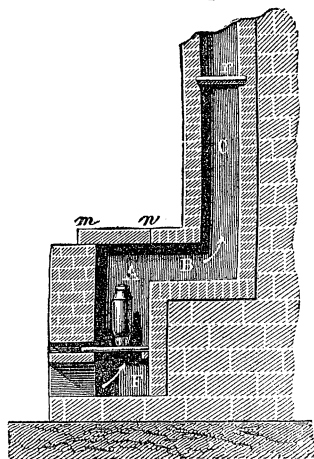


Fig. 514.

The crucibles, a vertical section of one of which is seen in fig. 515, are made of very refractory clay. One of the crucibles is placed in the furnace, covered with burning pit-coal, and the furnace is then filled with coke, merely to heat the sides of the furnace, the chimney, and the crucible. Thirty pounds of cemented steel, broken into pieces, are then introduced into the crucible, which is covered with its lid A, and the temperature is rapidly elevated. The fusion of the steel generally requires 4 hours, after which the crucible is removed, the lid taken off, and the fused steel poured into cast-iron ingot-moulds. The crucible is immediately replaced in the furnace, and a new charge introduced for a second fusion, which, however, requires only 3 hours. The same crucible may serve for a third melting, but is afterward rejected as useless.



Fig. 515.

A cast-steel of very superior quality, and known by the name *Wootz*, has long been manufactured in India. It is made in small

pieces, weighing at most from 2 to 4 lbs., by heating iron at a very high temperature in contact with certain vegetables which are carbonized by heat.

Steel remarkable for its great hardness is obtained by fusing ordinary steel with very small proportions of certain metals, such as silver and platinum.

§ 857. Steel, heated to a very high temperature, and then allowed to cool slowly, becomes as soft as cast-iron, and can be cut with a file, or turned in a lathe, but on being heated to redness and then suddenly cooled by dipping it into cold water, is rendered very hard and brittle. The steel, which is less dense than annealed steel, is then said to be *tempered*. By heating it again to redness and allowing it to cool slowly, it regains its original malleability.

Steel objects are first made of annealed steel, with the hammer, file, or lathe, and the proper degree of hardness is then given by tempering; but as they generally become too hard and brittle by this process, they must be again heated to bring them to a proper degree of softness. The great skill of the workman consists in knowing the exact moment of the completion of the annealing, in which he is guided by the often very brilliant colours displayed on the surface of the metal during the annealing, and which correspond exactly to certain temperatures. The colours are produced by thin pellicles of oxide reflecting various colours according to their thickness: in a word, the cause of this phenomenon is the same as that which produces the beautiful iridescence of a soap-bubble.

Tempered steel, reheated at 220° produces a straw-yellow colour.

“	“	240°	“	golden-yellow	“
“	“	255°	“	brown	“
“	“	265°	“	purple	“
“	“	285°	“	bright blue	“
“	“	295°	“	indigo-blue	“
“	“	315°	“	very deep blue	“

The reheating is carried to the production of any particular colour, according to the quality of the steel and the nature of the object.

Many cutting instruments are made by forging together bars of steel and soft iron, by which proceeding they are rendered less brittle, but also less hard, than those of pure steel. Gun-barrels are usually made in this manner.

When the surface of an object made of non-homogeneous steel is attacked by a feeble acid, the heterogeneous structure of the material is evinced, and different agreeable designs result, which vary according to the process adopted. The steel is then said to be *damasked*. When the steel is combined with small quantities of foreign metals, which are irregularly scattered through its substance, the effect of the figuring becomes very beautiful.



## TESTING OF IRON-ORES.

§ 858. The richness of an iron-ore may be ascertained, either by the dry or the humid way. Testing by the dry way is an imitation in miniature of the blast-furnace, and yields the same products, viz. cast-iron and slag, and has the advantage of allowing the operator to judge, by the small lump obtained in the assay, of the quality of cast-iron which the ore would produce in the blast-furnace.

Nevertheless, before making the assay in the dry way, some preliminary experiments in the humid way are generally performed, as they more clearly determine the nature of the ore, and show the quantity of flux necessary to be added to obtain a good smelting.

We shall divide the ores, which it may be necessary to assay, into four classes: 1st. Those ores which contain iron in the state of hydrated sesquioxide; 2d. Ores formed by anhydrous sesquioxide; 3d. Ores of magnetic oxide of iron; 4th. Sparry ores, that is, those formed by protocarbonate of iron.

1. The ores of the first class, which are much the most abundant in France, are tested in the following manner:

Ten grammes of the ore are first calcined to redness in a platinum crucible, to disengage water and carbonic acid. Let  $p$  be the weight of the calcined substance, then will  $(10-p)$  represent the weight of the water and carbonic acid.

Ten other grammes of finely powdered ore are then treated with very weak nitric acid, which dissolves only the carbonates of lime and magnesia which may be in the gangue. (If none existed, there would be no effervescence, and the use of the weak nitric acid would be superfluous.) When the effervescence has ceased, even after the addition of a fresh quantity of acid, the residue is collected on a small filter, washed with a little water, and calcined in a platinum crucible. If  $p'$  be the weight of this residue,  $(10-p')$  will represent the weight of the water, carbonic acid, and lime contained in the ore; and consequently,  $(p-p')$  will be the weight of the lime.

Lastly, 10 gm. of powdered ore are attacked with concentrated chlorohydric acid, and the solution boiled until the residue has entirely lost its colour. The quartz and clay, which alone remain as a residue, are collected on a filter and weighed after calcination. Their weight being represented by  $p''$ , we shall have for the composition of the ore, by collecting the results of all these operations:

Water and carbonic acid..... $(10-p)$

Lime ..... $(p-p')$

Quartz and clay..... $p''$

Oxides of iron and manga-

nese, (differentially)..... $10-(10-p)-(p-p')-p''=(p'-p'')$ .

If the ore contains only a small quantity of manganese, which is

easily recognised by the ochreous colour of its powder, the weight ( $p' - p''$ ) will represent pretty exactly the weight of the anhydrous sesquioxide of iron in the ore, and, consequently,  $\frac{7}{10} (p' - p'')$  will be the weight of the metallic iron.

It is more easy to make the assay by the dry way, under the most favourable conditions. Experiment has shown that the cast-iron most readily separates, and a well-fused slag, nearly entirely free from oxide of iron, is obtained when the gangue is composed of clay and carbonate of lime, in such proportions that the latter should be two-thirds of the clay. An addition of chalk or kaolin to 10 gm. of powdered ore is then made, until the mixture resembles the composition just indicated; which, after being well ground in an agate mortar, is introduced into the cavity *abc* of a crucible covered with damp charcoal\* (fig. 516). The ore is inserted in a heap *m* into the cavity made with a glass rod, and the crucible is filled with damp charcoal. The lid is luted with clay, and the crucible itself, being set on fire-bricks, or pieces of burnt

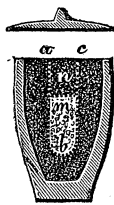


Fig. 516.

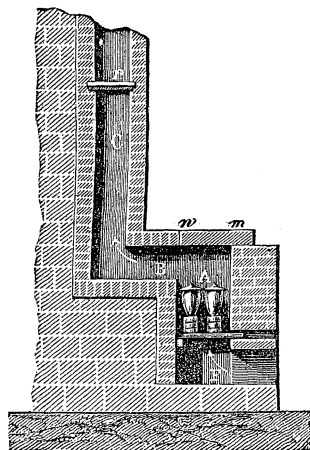


Fig. 517.

earth, and secured with clay, is heated in an air-furnace, or in a forge. Figure 517 represents the construction of an air-furnace very suitable for testing iron-ores; it resembles the furnace for melting steel (§ 856), but is smaller. Four crucibles may be arranged in this furnace, and 4 tests made at once. The fuel used is a mixture of equal parts of charcoal and coke, taking care to raise the temperature gradually, so that the crucibles may dry slowly, while the register *r* regulates the draught. During the last quarter of an hour the temperature is raised as high as possible. The operation lasts in all an hour and a quarter, after which the crucibles are removed and allowed to

\* The preparation of a "brasqued" crucible requires some precautions, which it may be worth while to indicate. "Brasque" is composed of charcoal, powdered and sifted, moistened with water so as to give it a certain degree of consistency, and introduced into a crucible of refractory clay, into which it is rammed with a wooden stamper. This requires several additions of the material, as it becomes compressed by pounding. Before adding a new layer, the surface of the preceding must be made rough, as otherwise it would not incorporate itself with the succeeding stratum, and the two layers might separate during the heating, causing cracks to form, through which the liquid substances might escape.

When the crucible is filled and the charcoal well-heaped in, a part of the "brasque" is removed with a knife, so as to form a rounded cavity *abc* (fig. 516), the material taken from which is heaped along the sides of the crucible; and the surfaces are then rubbed smooth with a strong glass rod.

VOL. II.—K

cool. The fused lump taken from the bottom of the crucible is composed of a button of cast-iron, surmounted by slag, both of which are weighed together. The slag is then broken off and pounded to pieces, to ascertain that it contains no metallic globules, and the button and globules are weighed.

It is proper to remark that as the metal weighed is in the state of cast-iron, that is, combined with a certain quantity of carbon, its weight is consequently rather too great; but at the same time this excess of weight nearly compensates for the small quantity of iron which always remains in the state of oxide in the slag.

Instead of the air-furnace of fig. 517, which is found only in laboratories where such tests are made in quantity, an ordinary blacksmith's forge may be used, when a sort of hearth can conveniently be made with refractory bricks, in the midst of which the crucible is to be placed.

Fig. 518 represents a small portable furnace, which may be constructed without much expense, and is well adapted for testing iron-ores. It is made of two large refractory crucibles *ABed*, *ABEF*, the upper one of which, forming the lid, has a large opening *O*, through which the fuel is charged and the air escapes, while the lower crucible has three holes *o*, *o'*, *o''*, and its bottom rests on a cup *U* of baked clay, into which the nozzle *a* of a bellows enters. The small "brasqued" crucible is, in order to place it in the middle of the furnace, set on several pieces of brick placed on each other, to the upper one of which it is luted with clay. The fuel used is charcoal or a mixture of charcoal and coke.

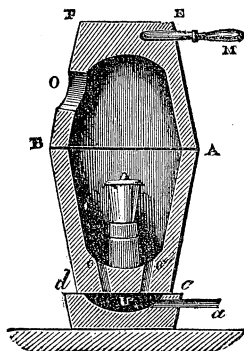


Fig. 518.

2. When the ore consists of anhydrous peroxide of iron, the proportion of siliceous gangue can no longer be determined by acting on it with chlorohydric acid, because the native peroxide is unaffected by this acid, and the latter therefore dissolves only the carbonate of lime, which may be thus determined:—In order to make the assay in the furnace,  $\frac{1}{3}$  of its weight of a fusible silicate, white glass, for example, is mixed with the ore, in order to prevent the too siliceous scorixæ from retaining oxide of iron. If this should nevertheless take place, which would be known by the deep green colour of the slag, the test must be repeated, but with an increased proportion of carbonate of lime, or with less glass than before.

3. As even the most concentrated acids act with difficulty on native magnetic iron, the proportion of quartzose gangue by which such ores are accompanied cannot be determined by chlorohydric

acid, and the assay must be made as in the preceding case, that is, the ore must be immediately fused in a forge-fire with an admixture of white glass and carbonate of lime.

4. Although the native protocarbonate of iron is converted by calcination into magnetic oxide, the loss of weight which sparry ores suffer by heat does not exactly represent the weight of the disengaged water and carbonic acid, because the protoxide of iron absorbs a portion of the oxygen of the carbonic acid which it decomposes. By treating the ore with weak nitric acid, the carbonate of lime is dissolved; but a certain quantity of iron being dissolved at the same time, the lime cannot be determined as in the first case, and it becomes necessary to act on the ore with concentrated boiling chlorohydric acid, in order to convert the iron into sesquioxide. The solution is evaporated to dryness at a gentle heat to drive off the excess of acid, and treated with water, which leaves the quartzose and argillaceous gangue undissolved; after which the sesquioxide of iron, the protoxide of manganese, and the lime are then successively separated in the liquid by the processes described § 803.

§ 859. When the oxide of iron readily dissolves in acids, the quantity of iron existing in an ore can be exactly and rapidly determined by boiling 3 grammes of the finely powdered ore with chlorohydric acid, until the solution loses its colour, evaporating to drive off the excess of acid, and treating the residue with water. The latter, which consists of the quartzose and argillaceous gangue, is collected on a filter and weighed. A standard solution of permanganate of potassa is then poured into the liquid, using the precautions indicated (§ 804), until the liquid assumes a permanent rose-colour, and the quantity of metallic iron existing in the 3 grammes of ore is determined from the quantity of permanganate of potassa used.

If the ore be specular iron, or magnetic oxide, it can only be acted on by chlorohydric acid, after being heated to a high red-heat in a platinum crucible, with 3 or 4 times its weight of carbonate of soda, or bisulphate of potassa. The peroxide of iron, in this way, becomes disaggregated and easier soluble in chlorohydric acid.

#### ANALYSIS OF CAST-IRON AND STEEL.

§ 860. Cast-iron is a compound of carbon with iron, frequently containing, in addition, a certain quantity of silicium, sulphur, phosphorus, and manganese. We shall proceed to describe the mode of successively determining these several elements.

*Determination of Carbon.*

§ 861. Gray cast-iron can be easily filed, while white cast-iron and fine metal are, on the contrary, very hard, but when the file will not cut them, they can be pounded in a mortar. Fig. 519

represents a small apparatus of cast-steel, in which the pulverization can be easily effected. It is composed of a steel receiver *abcd*, to which is fitted a cylinder *efgh*, exactly filled by a steel piston P. Some pieces of white cast-iron are placed in the cylinder, the piston P is introduced, and resting the base *bc* on an anvil, the head of the piston is struck with a hammer. After a certain number of blows, the powdered substance is removed, and passed through a silk sieve; the fragments then remaining on the sieve being again broken up in the apparatus, and this process repeated until the whole quantity is reduced to fine powder.

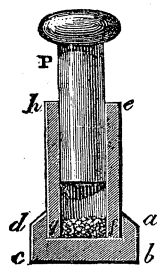


Fig. 519.

Five grammes of powdered cast-iron are then mixed with 100 or 120 gm. of chromate of lead,  $\frac{1}{4}$  of the mixture is set aside, and with the remaining  $\frac{3}{4}$ , 5 gm. of chlorate of potassa are intimately mixed, when the whole is introduced into a tube closed at one end, resembling those used for the combustion of organic substances with oxide of copper; and on it the mixture containing no chlorate of potassa is placed. The tube is rested on a sheet-iron grate, while a tube containing chloride of calcium, or pumice-stone soaked in concentrated sulphuric acid, to absorb the moisture given off by the materials, is fitted to its extremity, and the whole apparatus is then arranged as represented in fig. 279.

The anterior part of the combustion-tube, which does not contain chlorate of potassa, is first heated, and the coals are then slowly approached to that part containing the chlorate. The cast-iron burns, partly at the expense of the oxygen of the chromate of lead, and partly by that disengaged by the chlorate, and carbonic acid is formed and collected in the globe apparatus. Fresh coals are added, until the end of the tube is reached. The excess of oxygen gas arising from the decomposition of the chlorate is at the same time disengaged and driven through the apparatus; but a little experience soon teaches how to avoid any danger of an explosion. It is well to place a small quantity of a mixture of chromate of lead and chlorate of potassa at the end of the combustion-tube, as the oxygen disengaged from this drives the last traces of carbonic acid through the globe apparatus. The increase of weight of the latter gives very exactly the carbonic acid arising from the carbon of the cast-iron, while the sulphur it may contain

remains in the combustion-tube in the state of sulphate of lead, and does not affect the result of the experiment.

It is important to keep the mixture in the combustion-tube so that a free space may remain in the upper part of the tube, as otherwise the chromate of lead, on becoming doughy and expanded, might obstruct the tube and cause an explosion.

The same process necessarily applies to the determination of the carbon which exists in steel and in soft iron.

The carbon contained in cast-iron and steel may also be exactly determined by causing these substances to react slowly on chloride of silver. To do this, 30 or 40 grammes of chloride of silver are fused in a porcelain capsule, a piece of iron or steel weighing about 5 gm. and exactly weighed is placed on it, and then water containing a few drops of chlorohydric acid is added. The chloride of silver is gradually decomposed, while protochloride of iron is formed and the carbon set free; but the reaction is very slow, and often requires several weeks for its completion. There remains, at last, a spongy mass of carbon and silicic acid, from which the last traces of iron are extracted by boiling with dilute chlorohydric acid. The precipitate is collected on a filter and weighed after being well dried, or better still, after a calcination in a current of hydrogen gas. Its weight is that of the carbon and silicic acid united; and it is then calcined in a platinum capsule, by which the carbon burns off, when the weight of the silicic acid remaining can be directly determined, and that of the carbon calculated by the difference.

As a substitute for chloride of silver, chloride of copper may be employed, which acts more rapidly on the cast-iron, but always disengages a small quantity of carburetted gas, so that the weight of the carbon found is rather too small.

§ 862. We have seen that carbon could exist in cast-iron in two states: 1st, in that of combined carbon, as in white cast-iron and steel; 2dly, in the state of small isolated laminae, as in gray cast-iron. It is of the highest importance to distinguish these two states of carbon, as they exert a remarkable influence over the nature of the cast-iron, and moreover are easily determined by analysis. In fact, when chlorohydric acid is allowed to act on a white cast-iron or steel, the metal dissolves and evolves a very fetid hydrogen gas, containing a considerable quantity of gaseous carburetted hydrogen, and vapours of certain liquid carburetted hydrogens which have been not yet studied. All the carbon of the cast-iron disappears in these hydrogenated products, and the residue is composed only of the silicic acid produced by the silicium of the cast-iron. If, on the contrary, a gray cast-iron be treated with chlorohydric acid, the gas evolved is still fetid, as the carbon which was in intimate combination with the iron is converted into

gaseous or liquid carburets of hydrogen, but the isolated carbon which existed in it in the state of graphite remains intact with the silicic acid. The residue is collected on a small filter, and, after being well washed, is dried. Some ether is then poured over the filter, to dissolve any oil which may remain, after which it is again dried at a temperature above  $212^{\circ}$ , and the residue weighed: the weight of the graphite and silicic acid united is thus obtained. The substance is heated in a platinum capsule in the open air, or better still, in a current of oxygen, by which the graphite burns, and leaves as a residue only silicic acid, which can be determined by weight. By subtracting from the whole weight of the carbon obtained by the combustion of the cast-iron the weight of graphite first obtained, the weight of the combined carbon is ascertained.

*Determination of Silicium.*

§ 863. The silicium of cast-iron is determined by dissolving the latter in chlorohydric acid, which converts the silicium into gelatinous silicic acid. The liquid is evaporated to dryness to render the silex insoluble, then treated with water, and the residue collected on a filter. The silex is weighed, after having been calcined at a dull red-heat, and the weight of the silicium is deduced from it.

Cast-iron frequently contains particles of slag, so that the residue is composed not only of the silicic acid furnished by the silicium of the cast-iron, but also that of the slag, which may have been more or less altered by the chlorohydric acid. The slag of charcoal furnaces generally resists this acid, while that of coke furnaces is more or less completely acted on by it. By treating powdered cast-iron with weak chlorohydric acid, the iron may be entirely dissolved, without sensibly affecting the slag, while the residue consists of gelatinous silex and slag, and is treated by a solution of caustic potassa, which dissolves the silex and leaves the slag. The silicic acid which has been furnished by the silicium of the cast-iron can thus be exactly ascertained.

*Determination of Sulphur.*

§ 864. The cast-iron is acted on by aqua regia, which dissolves the iron as perchloride, and converts the sulphur into sulphuric acid. The liquid is diluted with water, and the sulphuric acid precipitated by chloride of barium as sulphate of baryta, from which the weight of the sulphur in the cast-iron may be deduced.

*Determination of Phosphorus.*

§ 865. The cast-iron is acted on by aqua regia, evaporated to dryness to drive off the excess of acid, and then treated with water. The liquid, containing phosphorus in the state of phosphoric acid, is

then allowed to digest at a temperature of about  $212^{\circ}$ , for several hours, with an excess of sulphhydrate of potassium, which precipitates iron and manganese in the state of sulphides. After separating these by filtration, the liquid contains phosphoric acid and alkaline sulphides, which are decomposed by a slight excess of chlorohydric acid, after which the liquid is boiled to drive off the sulphhydric acid. One decigramme of piano-forte wire is then weighed very exactly, dissolved in aqua regia, and added to the solution of perchloride of iron obtained. An excess of ammonia poured into the liquid then completely precipitates the iron added in the state of hydrated sesquioxide, and carries with it all the phosphoric acid which existed in the liquid, precipitated as a basic perphosphate of iron. This precipitate is weighed after calcination in the air; and if from it 0.143 gm., the weight of the sesquioxide of iron yielded by 0.100 gm. of metallic iron, are subtracted, the weight of the phosphoric acid, whence that of the phosphorous in the cast-iron may be deduced, is obtained.

The same determination may be made in the following manner:—After having dissolved the cast-iron in chlorohydric acid, the liquid is filtered and an excess of acetate of soda added, the acetic acid of which is set free and chloride of sodium is formed. Now, as sesquioxide of iron forms with phosphoric acid a phosphate  $\text{Fe}_2\text{O}_3 \cdot \text{PhO}_5$ , insoluble in acetic acid, the phosphoric acid combines with the proper quantity of sesquioxide of iron to form this phosphate, which is precipitated, collected on a filter, washed with boiling water, and weighed after calcination. The precipitate may also be redissolved in chlorohydric acid, the liquid boiled with sulphite of soda to bring the perchloride of iron to the state of protochloride, and the standard solution of permanganate of potassa poured in to determine the quantity of iron it contains. The weight of phosphoric acid is thence easily deduced, and, consequently, that of the phosphorus contained in the cast-iron.

#### *Determination of Manganese.*

§ 866. The manganese contained in cast-iron is easily ascertained by the processes described § 803.

#### ANALYSIS OF SLAGS AND FURNACE SCORIÆ.

§ 867. Slag is composed chiefly of silicates of alumina and lime, but often contains, in addition, small quantities of the silicates of iron and manganese. The various scoriæ arising from the refining of cast-iron are composed of silicates of iron and manganese, but may also contain small quantities of silicates of alumina, lime, and potassa, arising from the ashes of the fuel used. Forge scoriæ are readily acted on by concentrated chlorohydric acid, by which the ma-



jority of slags is, however, not attacked. These products are analyzed by the processes described in the analysis of glass (§ 704), except that, in the case of forge scoriæ, it is useless to employ carbonate of soda and fluohydric acid, as the substance is acted on immediately by chlorohydric acid.

#### REMARKS ON THE COMPOSITION OF IRON, STEEL, AND CAST-IRON.

§ 868. By the *hardness* of wrought-iron is understood the resistance it presents when filed, cut, bored, or struck with a hammer while it is cold, which properties vary greatly in the different kinds of iron manufactured in different furnaces. Iron which when cold readily takes the impression of the hammer, is commonly flexible and tough, but, although of an excellent quality, cannot be universally applied,—that which is, at the same time, hard and tough being preferred. The best iron is that which is very hard, without being brittle, that is, without breaking easily under the hammer.

Iron which breaks or splits easily when heated is said to be *short*; a defect which is produced by a small quantity of sulphur:  $\frac{1}{10000}$  part of sulphur will make iron slightly short.

When iron contains 0.5 per cent. of phosphorus, it is brittle when cold, while a smaller quantity only renders the metal harder, still giving iron of good quality.

Wrought-iron may contain 0.25 per cent. of carbon, without possessing the property of remarkably hardening by tempering, which is regarded as characteristic of steel (§ 857). When the carbon rises to 0.60 per cent. the metal becomes too steely, and strikes fire with a flint after tempering. The quantity of carbon which renders iron steely, varies with the purity of the metal; for very pure iron, for example, a larger proportion than for that containing smaller quantities of sulphur and phosphorus is required.

Steel, refined by fagoting, and which is, at the same time, sufficiently hard and tough for cutting instruments, contains from 1.0 to 1.5 per cent. of carbon. When the proportion of the latter is greater, the steel becomes harder, but loses in toughness and particularly in the property of being welded. Steel containing 1.75 per cent. of carbon cannot be welded at any temperature.

When iron is combined with 2 per cent. of carbon, it cannot be forged under the hammer. This property may be regarded as distinguishing steel from cast-iron, the compounds of iron with a greater proportion of carbon than 1.9, consequently, being no longer steel, but cast-iron.

Cast-steel which contains from 1.9 to 2 per cent. of carbon, cannot be forged, but it never parts with its graphite, even by very slow cooling. Graphite separates by slow cooling, only when the iron is combined with at least 2.5 per cent. of carbon.

The properties of cast-iron do not depend so much on the whole quantity of carbon contained, as on that with which it is intimately combined. Gray cast-iron most frequently contains only 2 or 2.5 per cent. of combined carbon, the rest of this substance being scattered through it in the form of graphitous spangles. Gray cast-iron requires a higher temperature for fusion than white cast-iron, and passes almost suddenly from the liquid to the solid state, while white iron passes through an intermediate doughy state; on which account, probably, white cast-iron is more easily refined than gray iron containing the same quantity of carbon. Therefore, it is always endeavoured to obtain white cast-iron for refining, when the purity of the ore and the fuel will allow it; for we have already said (§ 826) that with impure ores and fuels, the temperature of a blast furnace producing gray cast-iron must be greatly elevated, unless the gray iron be suddenly cooled on leaving the furnace.

Gray cast-iron is converted into white cast iron by sudden cooling, while the white passes into the gray state at a higher temperature, and by slow cooling.

## CHROMIUM.

EQUIVALENT = 26.7; (333.75, O = 100.)\*

§ 869. Chromium\* is obtained combined with a certain quantity of carbon, by heating, in a "brasqued" crucible, an intimate mixture of sesquioxide of chromium and 15 or 20 per cent. of carbon in a forge-fire, when the carburetted metal remains in the form of a porous lump, as the heat was not sufficient to fuse it. This metallic mass is finely powdered in a steel mortar, intimately mixed with a few hundredths of the green oxide of chromium, and the mixture heaped in a porcelain crucible accurately covered by its lid, which is then placed in a second earthen crucible, likewise "brasqued," and heated to the highest temperature of a forge-fire. The carbon of the carburetted chromium is burned by the oxygen of the oxide, and a purer metal is obtained, in the form of a gray agglutinated mass. This metal is brittle, but may be polished, and then displays a brilliant metallic lustre. It is very hard and scratches glass readily, and its specific gravity is about 6.0. It does not oxidize in dry air at the ordinary temperature, but combines rapidly with oxygen when heated to a dull red-heat. It dissolves in chlorohydric and dilute sulphuric acid with evolution of hydrogen gas.

Pure metallic chromium is obtained, in the form of a dark-gray powder, by decomposing the violet sesquichloride of chromium by potassium. The pulverulent metal has so powerful an affinity for oxygen, that it ignites before it reaches a dull red-heat, and is converted into green oxide of chromium when heated in contact with the air.

## COMPOUNDS OF CHROMIUM WITH OXYGEN.

§ 870. Chromium forms many compounds with oxygen:

1. The protoxide  $\text{CrO}$ , isomorphous with protoxide of iron  $\text{FeO}$ .
2. The sesquioxide  $\text{Cr}_2\text{O}_3$ , isomorphous with alumina and sesquioxide of iron  $\text{Fe}_2\text{O}_3$ .
3. An oxide  $\text{Cr}_3\text{O}_4$ , intermediate between the first two, and corresponding to magnetic oxide of iron  $\text{FeO}, \text{Fe}_2\text{O}_3$ ; so that its formula should be written  $\text{CrO}, \text{Cr}_2\text{O}_3$ .
4. Chromic acid  $\text{CrO}_3$ , corresponding to ferric acid  $\text{FeO}_3$ , and manganic acid  $\text{MnO}_3$ .
5. An intermediate oxide  $\text{CrO}_2$ , which should, however, rather

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\* Discovered in 1797 by Vauquelin.

be considered as a combination of chromic acid with protoxide of chromium:  $\text{CrO}, \text{CrO}_3$ .

6. Lastly, a perchromic acid  $\text{Cr}_2\text{O}_7$ , corresponding to permanganic acid  $\text{Mn}_2\text{O}_7$ .

*Protoxide of Chromium, CrO.*

§ 871. Protoxide of chrome is obtained by adding caustic potassa to a solution of protochloride of chromium, when a deep brown precipitate of hydrated protoxide is formed. But this substance has so great an affinity for oxygen that it decomposes water as soon as it is set free, disengaging hydrogen, and being converted into a tobacco-coloured powder, which is the hydrate of a *definite oxide*  $\text{Cr}_3\text{O}_4$ , corresponding to magnetic oxide of iron, and which should consequently assume the formula  $\text{CrO}, \text{Cr}_2\text{O}_3$ . The transformation takes place very rapidly, at the temperature of boiling water. The hydrate of the oxide of chrome  $\text{CrO}, \text{Cr}_2\text{O}_3$ , heated in a closed tube, is converted into the green oxide  $\text{Cr}_2\text{O}_3$ , with the evolution of hydrogen gas.

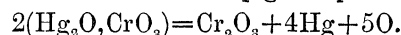
The composition of protoxide of chrome has never been directly ascertained, but has been inferred from the analysis of protochloride of chrome. This oxide contains

1 eq. chromium.....	26.7 or 333.7.....	78.53
1 “ oxygen.....	8.0	100.0.....21.47
1 “ protoxide.....	34.0	433.7.....100.00

*Sesquioxide of Chromium Cr<sub>2</sub>O<sub>3</sub>.*

§ 872. Sesquioxide of chromium is prepared in several ways :

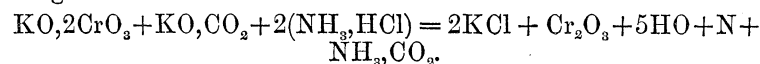
1. By heating protochromate of mercury  $\text{Hg}_2\text{O}, \text{CrO}_3$ ; when oxygen is disengaged, the mercury distils, and sesquioxide of chrome remains in the form of a deep-green powder :



2. By heating in a crucible a mixture of

1 part of bichromate of potassa,
$1\frac{1}{2}$ “ sal ammoniac,
1 “ carbonate of potassa,

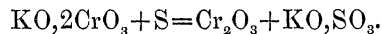
when chloride of potassium and oxide of chrome are formed, while the oxygen given off by the chromic acid combines with the hydrogen of the ammonia :



By treating the substance with water, the chloride of potassium is dissolved, leaving the sesquioxide of chrome in a state of purity.

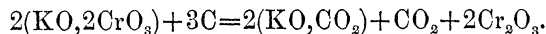
3. By heating at a suitable temperature, in an earthen crucible

or in a retort, 2 parts of bichromate of potassa, and 1 part of sulphur; when the sulphur forms, with the oxygen given off by the chromic acid, sulphuric acid, which combines with the potassa:

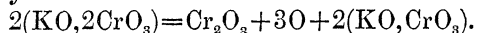


But an excess of sulphur is necessary, as a portion of this substance is volatilized without reacting on the chromate. By treating it with water, the oxide of chrome often remains mixed with a small quantity of sulphur, which may be expelled as sulphurous acid by heating it in contact with the air.

4. By calcining bichromate of potassa in a "brasqued" crucible, when carbonate of potassa, which is removed by water, and sesquioxide of chrome are formed:

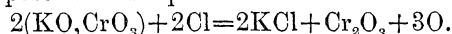


5. By heating bichromate of potassa to a high white-heat, when half of the chromic acid is decomposed into sesquioxide of chrome and oxygen, and a neutral chromate of potassa is formed, which is removed by water:



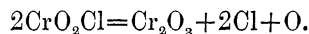
In this case the sesquioxide of chrome assumes the form of crystalline lamellæ.

6. By heating chromate of potassa to a red-heat, in a current of chlorine, when chloride of potassium is formed, and the chromic acid is decomposed into sesquioxide of chrome and oxygen:



Sesquioxide of chrome, thus prepared, appears in the form of green crystalline lamellæ.

7. Lastly, sesquioxide of chrome is obtained, in the form of small rhombohedral crystals, isomorphous with native crystallized alumina or corundum, by passing through a heated tube a red volatile liquid of the formula  $\text{CrO}_2\text{Cl}$ , which we shall describe under the name of *chlorochromic acid*.



The crystals which are deposited on the sides of the tube are often 1 or 2 millimetres in size, very brilliant, and of so deep a green colour as to appear black. They are as hard as corundum and readily scratch glass. Their specific gravity is 5.21.

Sesquioxide of chrome cannot be decomposed by heat. Hydrogen even does not reduce it at the highest temperature of our laboratory furnaces; but charcoal decomposes it in a forge-fire, when it is intimately mixed with the oxide. Vapour of sulphur does not act on it at a white-heat, while sulphide of carbon decomposes it at this temperature, and converts it into sulphide of chromium.

Sesquioxide of chrome imparts a green colour to fluxes, and we have already seen that this oxide is used for painting on glass and

porcelain. A red colour, called *pink-colour*, is also prepared with chrome, and was first used on porcelain by the English. It is obtained by heating to redness an intimate mixture of 100 parts of stannic acid, 34 of chalk, and 3 or 4 of chromate of potassa, and then treating the powdered material with chlorohydric acid until it has acquired a beautiful rosy tinge. The colouring principle of this substance is probably an oxide of chrome superior to the sesquioxide.

Strongly calcined, it combines with the acids, even when they are concentrated, only with great difficulty; the hydrate must therefore be dissolved when salts of the oxide are to be prepared.

In order to prepare the hydrated sesquioxide of chrome, a solution of the sesquichloride is precipitated by ammonia, when a gelatinous bluish-gray precipitate is formed, which must be washed with boiling water. The sesquichloride of chrome used in this preparation is obtained by decomposing bichromate of potassa by sulphurous acid, in the presence of an excess of chlorohydric acid. To effect this a current of sulphurous acid gas is passed through a concentrated hot solution of bichromate of potassa, mixed with chlorohydric acid, when the liquid soon changes in colour, becoming first brown, and subsequently assuming a beautiful emerald green hue. The reaction is terminated when the liquid still exhales a strong smell of sulphurous acid, after having been left to itself for several hours in a well-corked bottle.

Hydrated sesquioxide of chrome dissolves readily in acids. Moderately heated, it loses its water, still preserving the property of easily combining with acids; but if the temperature be further elevated, the substance suddenly becomes incandescent before reaching a red-heat, and, after incandescence, the oxide is nearly insoluble in acids.

§ 873. Sesquioxide of chrome can combine with powerful bases, and one of these compounds, found in nature, acquires great importance from being the ordinary chrome ore. It consists of sesquioxide of chrome and protoxide of iron, combined according to the formula  $\text{FeO}, \text{Cr}_2\text{O}_3$ : in mineralogy, it is called *chromate of iron*, or *chromic iron*. Chromic iron has sometimes been found crystallized in regular octahedrons, presenting, therefore, the same form as magnetic oxide of iron  $\text{FeO}, \text{Fe}_2\text{O}_3$ , and spinell  $\text{MgO}, \text{Al}_2\text{O}_3$ , which have similar formulæ. Most frequently, chromic iron forms considerable masses, of a deep gray colour and a greasy lustre; and its bearings resemble those of magnetic oxide of iron. The principal mines of chromic iron are in Sweden, the Ural, and near Baltimore in the United States.\* It has been found in

\* The most extensive and important locality by far, is that of Lancaster and Chester counties, Pennsylvania, which now supplies both the United States and Europe. A considerable part of the ore is now obtained by simply washing the sands of brooks.—*W. L. F.*

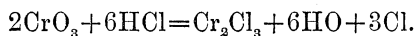
France, in the department of Var, but the mine appears nearly exhausted.

*Chromic Acid*  $\text{CrO}_3$ .

§ 874. In order to prepare chromic acid, one and a half times its volume of sulphuric acid is added gradually and in small quantities to a solution of bichromate of potassa, saturated at a temperature of from  $130^\circ$  to  $140^\circ$ , when bisulphate of potassa is formed, which remains in solution, and the liquid deposits on cooling long red needles of chromic acid. When the solution is cooled and the acid liquid decanted off, the crystals are allowed to drain in a funnel stopped with asbestos, and are then spread upon unburnt porcelain, which absorbs the remaining water. In order to purify them, their aqueous solution is treated with a small quantity of chromate of baryta, which combines with the sulphuric acid, and the filtered liquid is evaporated in vacuo.

Chromic acid is of a beautiful red colour at the ordinary temperature, but becomes almost black when heated. It decomposes before attaining a red-heat into sesquioxide of chrome and oxygen, and is deliquescent and very soluble, with an orange-yellow colour.

Chromic acid is a very powerful oxidizing agent: a few drops of absolute alcohol thrown on it, instantly convert it into sesquioxide, with so great an evolution of heat that the alcohol sometimes ignites. Hot concentrated sulphuric acid decomposes chromic acid, disengaging oxygen and forming sesquisulphate of chrome. Oxygen is sometimes prepared in the laboratory by heating together equal weights of bichromate of potassa and concentrated sulphuric acid. Chlorohydric acid converts chromic acid into sesquichloride of chrome, with disengagement of chlorine:



§ 875. Chromic acid appears to be able to combine in several proportions with sesquioxide of chromium. If a solution of bichromate of potassa be treated with sulphurous acid until it assumes a brown colour, and at that moment ammonia be added to the liquid, an ochreous precipitate is obtained, which hot water, after some time, decomposes into chromic acid which dissolves, and hydrated sesquioxide of chrome which remains. A similar compound is obtained by decomposing nitrate of chrome by a suitable degree of heat, when a brown spongy mass remains, of which the composition is represented by  $\text{CrO}_2$ , but to which the formula  $\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_3$  has been assigned.

*Perchromic Acid.*

§ 876. By treating chromic acid with oxygenated water, a beautiful blue solution is obtained, which, when shaken with ether, loses its colour, and imparts the blue compound to the ether.

This compound, which is not very stable, has not yet been obtained in an isolated state, nor has it been combined with the mineral bases. Its formula is supposed to be  $\text{Cr}_2\text{O}_7$ .

SALTS FORMED BY PROTOXIDE OF CHROME.

§ 877. Protoxide of chrome  $\text{CrO}$  is a powerful base, but nevertheless has been combined with only a small number of acids, on account of the difficulty of obtaining it pure, and the ready susceptibility of change of the salts themselves, which rapidly absorbing the oxygen of the air, are converted into sesquisalts. The acetate and the double sulphate of protoxide of chrome and potassa only are known; but in order to ascertain the distinctive characters of the protosalts of chrome, the protochloride must be resorted to. These compounds are known by the following reactions:—Caustic potassa at first affords a deep brown precipitate of hydrated protoxide, but which is immediately changed into a clear brown hydrated magnetic oxide, with the evolution of hydrogen gas. Sulfhydic acid does not precipitate them, while sulfhydrates yield a black precipitate. Bichloride of mercury gives a white precipitate of protochloride of mercury. Lastly, oxidizing reagents, such as chlorine, nitric acid, etc., immediately convert the protosalts of chromium into sesquisalts.

SALTS FORMED BY SESQUIOXIDE OF CHROME.

§ 878. Sesquioxide of chrome is a feeble base, analogous to sesquioxide of iron. The salts formed by this oxide may exist under two different modifications, which are distinguished by their colours, the first being violet, while the second is green. Several acids produce both modifications; but with others only one of the colours has hitherto been obtained.

A green and a violet sulphate are known. Ammonia forms in the solutions of these two salts precipitates which are distinguished by their shades of colour; the precipitate of the green sulphate being bluish gray, and producing a green solution with sulphuric acid, while that furnished by the violet modification is of a greenish gray, but also produces a green solution when treated with sulphuric acid.

Potassa and soda yield bluish-gray or greenish-gray precipitates, which dissolve in an excess of alkali, forming a green liquid, which loses its colour by boiling, as the hydrated oxide is again precipitated.

The alkaline carbonates give a greenish precipitate, perceptibly soluble in an excess of the reagent.

Sulfhydic acid does not precipitate the sesquisalts of chrome, but the sulfhydrates precipitate those of the hydrated sesquioxide.

The sesquisalts of chrome produce, like the protosalts, a glass



of a characteristic green colour when fused with borax. Fused with the alkaline carbonates, or better still, with the nitrates, they form alkaline chromates, which are recognised by the yellow solutions they produce, and by their great colouring power.

*Sesquinitrate of Chrome.*

§ 879. Hydrated sesquioxide of chrome dissolves immediately in nitric acid, furnishing a green solution which leaves, after evaporation, a very soluble green salt, readily decomposable by heat. At a moderate temperature, it yields a brown substance, which is regarded as a sesquichromate of chrome  $\text{Cr}_2\text{O}_3, \text{CrO}_3$ .

*Sesquisulphates of Chrome.*

§ 880. The neutral sesquisulphate of chrome  $\text{Cr}_2\text{O}_3, 3\text{SO}_3$  has been obtained with three different colours, violet, green, and red, which appear to correspond to three modifications of the salt.

The *violet sulphate* is obtained, by leaving for several weeks, in a badly-corked bottle, 8 parts of hydrated sesquioxide of chrome, dried at  $212^\circ$ , and 8 or 10 parts of concentrated sulphuric acid. The solution, which is at first green, gradually becomes blue, and, after some time, a greenish-blue crystalline mass is deposited. With an aqueous solution of this substance, alcohol gives a violet-blue crystalline precipitate, which, after having been dissolved in very weak alcohol, is left to itself. After some time, the liquid deposits small regular octohedrons of the formula  $\text{Cr}_2\text{O}_3, 3\text{SO}_3 + 15\text{HO}$ .

The *green sulphate* is prepared by dissolving sesquioxide of chrome, at a temperature of  $120^\circ$  to  $140^\circ$ , in concentrated sulphuric acid, or by boiling the solution of the violet sulphate. The liquid, when rapidly evaporated, yields a green crystalline salt, having the same composition as the violet sulphate. The green sulphate readily dissolves in alcohol with a blue colour, while the violet sulphate is insoluble in it. The violet and green sulphates are also distinguished by several chemical reactions; thus, the cold solution of the green sulphate is not completely decomposed by the soluble salts of baryta, and the decomposition is complete only when the liquid is boiled, while all the sulphuric acid of the violet solution may, on the contrary, be precipitated when cold by salts of baryta.

If the violet or green sulphate be heated to a temperature of  $392^\circ$ , with an excess of sulphuric acid, a clear yellow mass is obtained, which leaves as a residue the *red* neutral sulphate of chrome, after the evaporation of the excess of acid. This anhydrous sulphate is insoluble in water, and dissolves with difficulty even in acid liquids.

*Chromic Alums.*

§ 881. Sesquisulphate of chrome is isomorphous with sulphate of alumina, and may take the place of the latter in the alums. The crystallizable chromic alums contain the violet modification of sulphate of chrome. Three of these alums are known, affording beautiful crystals :

Potassic alum.....  $\text{Cr}_2\text{O}_3 \cdot 3\text{SO}_3 + \text{KO} \cdot \text{SO}_3 + 24\text{HO}$ .

Sodic alum.....  $\text{Cr}_2\text{O}_3 \cdot 3\text{SO}_3 + \text{NaO} \cdot \text{SO}_3 + 24\text{HO}$ .

Ammoniacal alum.....  $\text{Cr}_2\text{O}_3 \cdot 3\text{SO}_3 + (\text{NH}_3, \text{HO})\text{SO}_3 + 24\text{HO}$ .

*Potasso-chromic alum* is prepared by heating slightly a mixture of bichromate of potassa and sulphuric acid dissolved in water, with a reducing substance, such as sugar, alcohol, etc.; or by passing a current of sulphurous acid through the liquid. The solution deposits by spontaneous evaporation, or even on cooling, if it be sufficiently concentrated, large regular octahedrons, like those of ordinary alum, of a deep violet red. They dissolve readily in water, with a dirty violet colour, but are insoluble in alcohol. Heated to  $176^\circ$ , the solution becomes green, and deposits by evaporation red crystals of alum, but leaves as a residue an uncrystallized mass, which is still a double sulphate of potassa and chrome, but which no longer presents any of the characters of potassa-chromic alum. The solutions of the green sulphates of chromium give the same green product when they are evaporated with sulphate of potassa.

## CHROMATES.

§ 882. Chromic acid combines with nearly all the bases, forming with the alkalies salts which crystallize perfectly, and are isomorphous with the corresponding sulphates. The chromates of strontian, lime, and magnesia are soluble, while the other metallic chromates are insoluble, or nearly so.

Chromic acid forms with the alkalies two series of salts: neutral chromates and bichromates, the former of which are of a bright yellow colour, while the bichromates are orange-red. The soluble chromates are easily distinguished: first, by their colour, which is very decided, even in very dilute solutions; and also, by the characteristic colours of the precipitate they yield with various metallic salts. They form a yellow precipitate with the salts of lead and bismuth, a bright red one with those of mercury, and a deep red one with those of silver. The chromates, heated with concentrated chlorohydric acid, give a green solution of sesquichloride of chrome.

*Chromates of Potassa.*

§ 883. The compounds of chromic acid with potassa are the most important products of chrome, as large quantities of them are used in dyeing and calico-printing. They are obtained directly from

chrome-ore, that is, from chromic iron. The chrome-ore, which even when purified by washing always contains a certain quantity of quartzose and aluminous minerals, is heated, finely powdered, in a reverberatory furnace, with carbonate of potassa, to which some nitrate of potassa is frequently added, and the material is constantly stirred to facilitate its oxidation. Chromate of potassa, but at the same time, a certain quantity of silicate and aluminate of potassa, are formed, to separate which the roasted substance is treated with water, which dissolves the soluble alkaline salts, after which acetic acid is added to the liquid until it assumes an acid reaction, which is a sign that the neutral chromate of potassa is converted into a bichromate and that the silicic acid is deposited. The bichromate, being much less soluble than the neutral salt, is easily separated by crystallization, and purified by recrystallization.

Bichromate of potassa forms beautiful red crystals, which fuse without change before attaining a red-heat, but decompose at a higher temperature into neutral chromate, sesquioxide of chrome, and oxygen which is given off. This salt contains no water of crystallization, and is soluble in 10 parts of cold and in a much less quantity of boiling water.

Neutral chromate of potassa is obtained by adding chromate of potassa to a solution of the bichromate until the latter assumes a clear yellow colour, and evaporating the liquid, when yellow anhydrous crystals are obtained, presenting exactly the same form as sulphate of potassa. The neutral chromate is very soluble, as cold water dissolves more than double its weight of it, and hot water still more. The solution of the neutral chromate of potassa turns the red tincture of litmus blue.

The neutral chromate of soda is very soluble in water, and, during cooling from a hot saturated solution, forms crystals corresponding to the formula  $\text{NaO}, \text{CrO}_3 + 10\text{HO}$ , and is isomorphous with sulphate of soda  $\text{NaO}, \text{SO}_3 + 10\text{HO}$ .

*Bichromate of Chloride of Potassium, or Chlorochromate of Potassa.*

§ 884. If a solution of bichromate of potassa be boiled with chlorohydric acid until chlorine begins to be evolved, a brown liquid is obtained, which on cooling deposits beautiful orange-coloured crystals of a salt which may be regarded as a bichromate of chloride of potassium  $\text{KCl}, 2\text{CrO}_3$ . This substance may also be considered as a bichromate of potassa, in which one of the equivalents of chromic acid is replaced by 1 equiv. of chlorochromic acid,  $\text{CrO}_2\text{Cl}$ ; but then its formula should be written,  $\text{KO}(\text{CrO}_3 + \text{CrO}_2\text{Cl})$ .

*Chlorochromic Acid.*

§ 885. A chlorochromic acid  $\text{CrO}_2\text{Cl}$  may be obtained isolated, by fusing in an earthen crucible 10 parts of sea-salt and 17 parts of bichromate of potassa. The liquid matter is run on a sheet-iron

plate, and, when cool, broken into fragments, which are introduced into a glass retort with 30 parts of concentrated sulphuric acid. Reaction commences immediately, a gentle heat is subsequently applied, and a blood-red liquid condenses in the receiver, which should be cooled with ice. The density of this liquid is 1.71; it boils at  $248^{\circ}$ . By contact with water it is decomposed into chromic and chlorohydric acids:  $\text{CrO}_2\text{Cl} + \text{HO} = \text{CrO}_3 + \text{HCl}$ . It should be kept in glass tubes hermetically sealed.

#### COMPOUND OF CHROMIUM WITH SULPHUR.

§ 886. If sulphide of carbon in vapour be passed through a heated porcelain tube containing sesquioxide of chrome, the latter is converted into crystalline spangles of sulphide of chromium  $\text{Cr}_2\text{S}_3$ , resembling native graphite.

#### COMPOUND OF CHROMIUM WITH NITROGEN.

§ 887. A compound of chromium with nitrogen is obtained by heating sesquichloride of chrome in a current of dry ammoniacal gas. This substance then presents the form of a brown powder, which is unchangeable in the atmosphere at the ordinary temperature, but readily ignites and is converted into sesquioxide when heated in the air.

#### COMPOUNDS OF CHROMIUM WITH CHLORINE.

§ 888. Chromium forms two compounds with chlorine: a protochloride  $\text{CrCl}$ , corresponding to the protoxide  $\text{CrO}$ ; and a sesquichloride  $\text{Cr}_2\text{Cl}_3$ , corresponding to the sesquioxide  $\text{Cr}_2\text{O}_3$ , and capable of existing under two different modifications.

*Protochloride of chrome*  $\text{CrCl}$  is obtained by passing hydrogen gas over anhydrous sesquichloride heated to redness in a porcelain tube. Protochloride of chrome is white, dissolves in water, yielding a blue solution, which absorbs rapidly the oxygen of the air, thus converting the protochloride into an oxychloride  $\text{Cr}_2\text{Cl}_2\text{O}$ . The solution of protochloride of chrome readily absorbs deutoxide of nitrogen, like the protochloride and protosulphate of iron.

§ 889. Anhydrous *sesquichloride of chrome* is prepared by heating an intimate mixture of sesquioxide of chrome and charcoal in a current of dry chlorine, the process otherwise exactly resembling that for the preparation of chloride of aluminum (§ 604). The sesquichloride is deposited in the anterior part of the tube, in the form of small spangles of a peach-blossom colour. Anhydrous sesquichloride of chrome may be brought in contact with water without being dissolved by it in the slightest degree, but boiling water dissolves it after some time, giving a green solution. If a very small quantity of protochloride of chrome  $\text{CrCl}$  be added to cold water, sesquichloride immediately dissolves with evolution of heat, and yields a green solution identical with that obtained by

dissolving hydrated sesquioxide of chrome in chlorohydric acid. The smallest quantity of protochloride of chrome,  $\frac{1}{10000}$ , is sufficient to produce this remarkable effect.

By dissolving hydrated sesquioxide of chrome in chlorohydric acid, a green solution is obtained, which yields, on evaporation, a deliquescent green mass, the formula of which, when evaporated in dry air, is  $\text{CrCl}_3 + 9\text{HO}$ . Heated, it evolves water and chlorohydric acid, while oxychlorides remain. Some chemists regard this body as resulting from the direct combination of chlorohydric acid with sesquioxide of chromium, as a *chlorohydrate of sesquioxide of chrome*, and give it the formula  $\text{Cr}_2\text{O}_3, 3\text{HCl} + 6\text{HO}$ . If the hydrated sesquichloride be heated in a current of chlorohydric acid gas, it only loses its water, and is converted into a violet anhydrous sesquichloride.

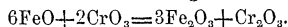
By pouring chloride of barium into a solution of violet sulphate of chrome, sulphate of baryta is precipitated, and there remains in the liquid a violet sesquichloride of chrome, presenting the same composition as the green sesquichloride. These two modifications are observed in several chemical reactions; thus nitrate of silver only precipitates when cold  $\frac{2}{3}$  of the chlorine of the green chloride, while the violet sesquichloride immediately parts with the whole of it at the boiling point. The violet chloride is rapidly transformed into the green chloride.

#### DETERMINATION OF CHROME; AND ITS SEPARATION FROM THE METALS PREVIOUSLY STUDIED.

§ 890. Chrome is always determined in the state of green oxide. To do this, the chrome is converted into chloride or sulphate of sesquioxide, and the boiling solution is precipitated by ammonia. The gelatinous precipitate of the hydrate is collected on a filter, and, after being well washed, is calcined in a closed platinum crucible.\*

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\* A much more exact method is the alkalimetric determination of chrome, which depends on the same principle as that of peroxide of manganese, described in the note to § 765. The chrome must first be converted into chromic acid, unless it be already in that state, by a fusion with caustic potassa and chlorate of potassa. Chlorohydric acid being added to the solution of the chlorate formed, the latter is then reduced by a protosalt of iron according to the formula,



Now, if a certain quantity of a protosalt of iron has been added, and the surplus of this be determined by permanganate of potassa, according to § 804, the quantity of chromic acid or oxide may be found by the above formula; as six equivalents of the protoxide of iron found by subtracting the quantity determined from the whole quantity added, correspond exactly to two equivalents of chromic acid, or to one of sesquioxide of chrome.

The protosalt of iron employed is the protosulphate of iron and ammonia, of which a standard solution is kept for the determination of peroxide of manganese.

The methods of determining chrome by weight are inexact; as sesquioxide of chrome cannot entirely be freed from a part of the fixed alkali used for its pre-

When chrome exists in solution as chromic acid, nitrate of mercury is added, and the precipitate of chromate of mercury formed is calcined in a platinum crucible, leaving sesquioxide of chrome, which is weighed. Chromic acid may, also, be converted into sesquichloride of chrome, by heating the liquid with chlorohydric acid, and passing a current of sulphurous acid gas through it, when oxide of chrome may be precipitated by ammonia.

When the oxide of chrome exists in the state of a salt mixed with alkaline or alkalino-earthly salts, it is precipitated when hot by caustic ammonia, which only precipitates the oxide of chrome, and is filtered rapidly, so as to avoid, as much as possible, the contact of the air, in order that the carbonic acid of the air may not precipitate the alkaline earths. If the liquid contains manganese, an ammoniacal salt must first be added in sufficient quantity to prevent the magnesia from being precipitated by the ammonia. The oxides of chrome and the alkaline earths may also be precipitated by an alkaline carbonate, but the mixture must then be fused in a platinum crucible with carbonate of soda, when chromate of soda is formed which is dissolved in water. The chrome is then precipitated by the processes described.

Oxide of chrome is separated from alumina by boiling the hydrated oxides with caustic potassa, which dissolves only the alumina.

Oxide of chrome is separated from oxide of manganese by adding to the liquid containing the two oxides a quantity of ammoniacal salt sufficient to prevent the oxide of manganese from being precipitated by the ammonia. The liquid is then boiled, and an excess of ammonia added, which completely precipitates the oxide of chrome.\*

In order to separate oxide of chrome from the oxides of iron, the substance must be heated with caustic potassa in a silver crucible, when chromate of potassa is formed, which is dissolved in water, leaving the peroxide of iron isolated.

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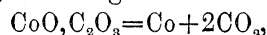
precipitation, and ammonia does not precipitate it perfectly; and the other method, not mentioned in the text, of precipitating chromic acid by acetate of lead, and weighing the chromate of lead formed, has the disadvantage that chromate of lead is not absolutely insoluble in water.—*W. L. F.*

\* By far the best method of separating chrome from manganese is to precipitate the former as sesquioxide by carbonate of baryta, which leaves the manganese in solution.—*W. L. F.*

## COBALT.

EQUIVALENT = 29.5 (369.0; O = 100).

§ 891. Pure metallic cobalt\* is obtained by reducing its oxides in a current of hydrogen gas; but the metal is then in the form of a black powder which is pyrophoric, like oxide of iron under the same circumstances: it becomes incandescent when projected in contact with the air. The metal is obtained in a more aggregated and less oxidizable form, by making the reduction by hydrogen at a higher temperature, in a porcelain tube heated in a reverberatory furnace. The oxides of cobalt, like those of iron, are easily reduced by cementation in contact with charcoal. If oxide of cobalt be heaped in a "brasqued" crucible, and heated in a forge-fire, precisely as in the assay of iron, a fused metallic lump of carburetted cobalt is obtained, which is gray, possessing a lustre resembling that of cast-iron; but it has but little malleability, and breaks under the hammer. Pure fused metallic cobalt may be obtained by adopting a process which does not succeed for iron. Oxalate of cobalt is heaped in a porcelain tube closed at one end, so as to introduce as great a quantity as possible; and this tube, closed with a lid, is placed in an earthen crucible, and the whole is then heated in a strong forge-fire, after the interstices have been filled with clay. The oxalate of cobalt is decomposed with evolution of carbonic acid, according to the reaction,



when the metallic cobalt alone remains, and, if the temperature be sufficiently high, fuses into a button. The cobalt thus obtained is of a steel-gray colour, susceptible of a fine polish, and of the specific gravity 8.5. Cobalt is nearly as magnetic as iron.

Cobalt is less affected by damp air than iron, but after some time becomes covered with a brownish-black rust. Heated in the air, it is converted into an oxide.

Cobalt dissolves in chlorohydric and dilute sulphuric acids, with disengagement of hydrogen gas; but the solution is effected more slowly than that of iron or zinc.

## COMPOUNDS OF COBALT WITH OXYGEN.

§ 892. Cobalt forms two well defined oxides: a protoxide containing 21.32 per cent. of oxygen, and a sesquioxide containing for the same quantity of metal one and a-half times more oxygen.

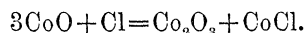
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\* Cobalt was first obtained in the metallic state by Brandt, in 1733.

The equivalent of cobalt, deduced from the composition of these oxides by giving to the protoxide the formula  $\text{CoO}$ , is 29.5.

Hydrated *protoxide of cobalt* is obtained by adding caustic potassa to the solution of a salt of cobalt, a sulphate or a nitrate for example. The gelatinous precipitate, of a lavender-blue colour, should be well washed with boiling water to remove the last traces of potassa, and calcined protected from the air. The protoxide is also prepared by calcining carbonate of cobalt in a close crucible. Protoxide of cobalt is a powder of a deep ash-gray colour, which, when heated in the air, absorbs oxygen, and appears to be converted into an oxide  $\text{CoO} + \text{Co}_2\text{O}_3$ , corresponding to magnetic oxide of iron. It is a powerful base, which forms red salts, isomorphous with those yielded by the other metallic oxides of the same formula.

*Sesquioxide of cobalt* is obtained by passing a current of chlorine through water containing hydrated protoxide in suspension; when the liquid becomes rose-coloured and a black precipitate is formed. Under these circumstances, a portion of the protoxide is changed into a chloride, which dissolves, and parts with its oxygen to another portion of the protoxide, which is changed into sesquioxide:



The whole of the protoxide may be converted into sesquioxide by precipitating the dissolved protochloride by potassa, and again passing chlorine through the liquid; which is the same as immediately treating the hydrated protoxide by a solution of an alkaline hypochlorite.

#### SALTS FORMED BY PROTOXIDE OF COBALT.

§ 893. The protosalts of cobalt are generally of a currant-red or peach-blossom colour. Their solutions are of a currant-red; but some of them, principally that of the protochloride, are red only when diluted, and change to a bright blue when concentrated, owing to a dehydration of the salt, or to an isomeric modification. It also occurs when the temperature is elevated. Crystals of chloride of cobalt, when cold, are rose-coloured, but when slightly heated, assume a beautiful blue, without perceptibly losing any water; for they return to the rose colour on cooling. Characters written upon paper with a dilute solution of chloride of cobalt, disappear after the evaporation of the water, because the chloride of cobalt is then in its rose-coloured modification; but if the paper be brought near to the fire, the chloride is transformed by the elevation of temperature into its blue modification, by which the characters become apparent, as the colour of this modification is deeper. As the paper cools, the characters disappear again entirely, unless the paper has been too highly heated.

This property of chloride of cobalt has given it some celebrity as a *sympathetic ink*.



The characters only become blue if the chloride of cobalt used is very pure; but when it contains a small quantity of nickel they turn green: the purity of the liquid may thus be ascertained.

Salts of cobalt yield, with potassa and soda, lavender-blue precipitates. Ammonia does not precipitate the solutions containing an excess of acid, as a double ammoniacal salt, not decomposable by an excess of ammonia, is then formed.

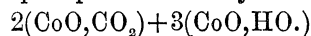
The alkaline carbonates produce a rose-coloured precipitate of carbonate of cobalt, while the alkaline phosphates and arseniates throw down peach-blossom coloured precipitates readily soluble in an excess of acid. Yellow prussiate of potash gives a dirty-green precipitate. When the salts of cobalt contain an excess of acid they are not precipitated by sulphuric acid. The alkaline sulphates afford a black hydrated sulphide.

*Sulphate of cobalt* is obtained by dissolving the oxide in sulphuric acid, and crystallizes, at the ordinary temperature, with 7 equivs. of water  $\text{CoO}, \text{SO}_3 + 7\text{HO}$ , in the same form as sulphate of iron. The formula of the crystals formed between  $68^\circ$  and  $86^\circ$  is  $\text{CoO}, \text{SO}_3 + 6\text{HO}$ , and they are isomorphous with sulphate of magnesia.

*Nitrate of cobalt* is obtained by dissolving the metal, or the oxide, in nitric acid. The nitrate is easily decomposed by heat, and leaves, when subjected to a moderate temperature, the oxide  $\text{CoO}, \text{Co}_2\text{O}_3$  as a residue.

*Oxalate of cobalt* is deposited in small rose-coloured crystals, when oxalic acid is added to a solution of sulphate of cobalt. The salt is but slightly soluble in water.

The alkaline carbonates produce in solutions of the salts of cobalt a pale rose-coloured precipitate of the hydrocarbonate



#### COMPOUND OF COBALT WITH SULPHUR.

§ 894. *Sulphide of cobalt* is prepared by heating the oxide with an alkaline polysulphide: if the calcination be carried to a white-heat, a bronze-coloured metallic button is obtained.

#### COMPOUND OF COBALT WITH CHLORINE.

§ 895. Chloride of cobalt is prepared by dissolving the oxide in chlorohydric acid. We have already said that this chloride exists under two modifications, as a rose-coloured, and as a blue compound.

#### COMPOUNDS OF COBALT WITH ARSENIC.

§ 896. Two crystallized arseniurets of cobalt are found in nature; but these minerals generally contain at the same time arseniurets of nickel and iron. Cobalt is also found in combination, at the

same time, with arsenic and sulphur, in the state of a sulfarseniuret  $\text{CoAs}_2 + \text{CoS}_2$ : mineralogists call it *gray cobalt*. Its most ordinary crystalline form is the *cuvo-octahedral*. The gray cobalt worked at Tunaberg, in Sweden, which is very pure, is mostly used in laboratories to obtain the products of cobalt. To effect this, the powdered ore is first roasted in the muffle of a cupelling-furnace, with a gentle heat at the commencement, in order to avoid the fusion of the material, when the sulphur burns to sulphurous acid, a large portion of the arsenic is changed into arsenous acid which is disengaged in white fumes, and another portion of the arsenic is transformed into arsenic acid which remains in combination with the oxidized cobalt, forming arseniate of cobalt. When white fumes are no longer disengaged, a small quantity of powdered charcoal is thrown on the material, and the whole is mixed; after which the door of the muffle is closed, when the charcoal reduces the arseniate to the state of an arseniuret; and, if air be admitted, the roasting recommences and removes an additional quantity of arsenic. As this substance, however, cannot be entirely separated in this way, the whole must be roasted with carbonate of soda and a small quantity of nitre, and then heated in a crucible, when the last portions of arsenic combine with the soda, forming arseniate of soda, which is removed by treating the material with boiling water. The cobalt remains in the state of an oxide, generally containing a small quantity of peroxide of iron, which is separated by dissolving in nitric acid, evaporating to drive off the excess of acid, and then treating with water. A few drops of carbonate of soda added to the liquid precipitate hydrated peroxide of iron. Lastly, the oxide of cobalt is obtained by adding caustic potassa; or, when metallic cobalt is to be prepared, the oxalate intended for this purpose is obtained by an addition of oxalic acid.

The powdered ore may also be immediately fused with a mixture of carbonate of soda and sulphur, when a sulfarseniate of sodium and sulphide of cobalt are formed, which collect at the bottom of the crucible in the form of a ball. This sulphide, heated with dilute sulphuric acid, dissolves by disengaging sulphydric acid, yielding a solution of sulphate of cobalt.

#### DETERMINATION OF COBALT; AND ITS SEPARATION FROM THE METALS PREVIOUSLY STUDIED.

§ 897. Cobalt is determined either as protoxide or in the metallic state. It is generally precipitated from its solutions by caustic potassa, when the precipitate, being washed with boiling water and calcined at a strong red-heat in a close platinum crucible, leaves protoxide of cobalt; but it is always to be feared that a portion of the cobalt may remain in the state of sesquioxide. It is, therefore, best to place the oxide in a glass bulb A (fig. 520), and heat it in a current of hydrogen gas, thus restoring the oxide to

VOL. II.—M

the state of metallic cobalt, which is weighed as such. When the

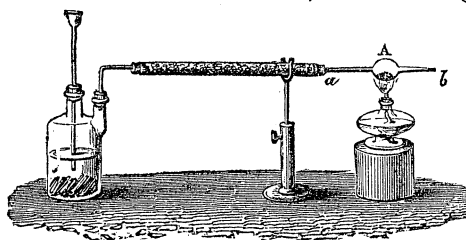


Fig. 520.

liquid contains ammoniacal salts, it must be evaporated to dryness with excess of potassa to drive off the ammonia, and then treated with water. Cobalt may also be precipitated as sulphide by sulphhydrate of ammonia; but the sulphide must then

be redissolved in nitric acid, and the oxide precipitated by potassa.

§ 898. Cobalt is separated from the alkaline and alkalino-earthly metals by sulphhydrate of ammonia, which precipitates the cobalt alone as sulphide. If the solution contains magnesia, care must be taken to add an ammoniacal salt, to prevent the precipitation of this substance.

The separation of the oxides of cobalt and alumina is easily effected by caustic potassa in excess, which dissolves the alumina and precipitates the oxide of cobalt.

It is very difficult satisfactorily to separate cobalt from manganese. The best method is to heat the two oxides, first in a current of chlorohydric acid gas, which transforms them into chlorides, and then in a current of hydrogen, which restores the chloride of cobalt to the metallic state, but does not decompose the chloride of manganese; when, by treatment with water, the latter chloride only is dissolved.

In order to separate cobalt from iron, the iron is brought to the state of peroxide, and enough sal-ammoniac added to prevent the precipitation of the cobalt by an excess of ammonia, which throws down only the sesquioxide of iron: the cobalt is then precipitated in the filtered liquid by sulphhydrate of ammonia.

#### SMALT, AZURE, OR ZAFFRE.

§ 899. Oxide of cobalt readily combines with fusible silicates, producing beautiful blue glasses, which find an extensive use in porcelain-painting, and are highly valued for their property of resisting the highest temperatures, provided no deoxidizing substances be present.

A blue glass containing oxide of cobalt is technically prepared, which, when finely powdered, is used for colouring wall and writing paper, and for bluing linen. This glass, called *smalt*, or *azure*, is manufactured in large quantities, from the native sulfarseniuret of cobalt, in Saxony and other parts of Germany. The ore is roasted in a reverberatory furnace, in which the vapours of arsenious acid condense in the pipes just below the return-chimney. The ore, properly roasted, is mixed with white sand and very pure carbonate

of potassa, in determinate proportions, and fused in glass-house pots. A metallic button, which is called *speiss*, composed chiefly of arseniurets of nickel and iron, is often deposited at the bottom of the pot. The vitreous substance, which has an intense blue colour, is pounded after cooling, and then ground to a fine powder, which is then suspended in water, when the grosser particles are first deposited, and must again be ground. The supernatant muddy waters are decanted after some time, and poured into buckets, where they gradually deposit finer and finer powder. The clearness of the blue colour depends on the fineness of the particles.

#### COBALT-BLUE, OR THENARD'S BLUE.

§ 900. Oxide of cobalt also enters as a colouring principle into another colour used in painting, and called *cobalt-blue*, or *Thenard's blue*. This colouring matter is prepared as follows:—A solution of sulphate or nitrate of cobalt is precipitated by phosphate of potassa; and, on the other hand, a solution of alum is treated with carbonate of soda. The two gelatinous precipitates of alumina and phosphate of cobalt are intimately mixed, in the proportion of 3 volumes of phosphate, and from 12 to 15 parts of alumina; when the mixture, dried and calcined in a crucible, changes into a beautiful blue powder. It is important to prevent the combustible vapours of the furnace from entering the crucible, as they would seriously injure the shade. This inconvenience is avoided with certainty by placing at the bottom of the crucible a small quantity of oxide of mercury, which produces an atmosphere of oxygen gas, and preserves the oxide of cobalt from reduction.

## NICKEL.

EQUIVALENT = 29.6 (370.0; O = 100.)

§ 901. Metallic nickel\* is obtained in precisely the same manner as cobalt. Oxide of nickel, reduced by oxygen at a low temperature, yields a pulverulent metal, which becomes incandescent in the air, and, when reduced in a "brasqued" crucible in a forge-fire, produces a well-fused carburetted metal. Pure melted metallic nickel is obtained by heating oxalate of nickel in a closed vessel in a strong forge-fire.

Nickel is a slightly-grayish white metal, which is so much more malleable than cobalt, that it can be hammered and drawn out into fine wire. Its density is about 8.8. It is nearly as magnetic as iron, but loses this property when heated to about 400°. Nickel bears pretty well the contact of a damp atmosphere, but by heating in the air is converted into an oxide. It dissolves in chlorohydric and dilute sulphuric acids, with disengagement of hydrogen gas.

## COMPOUNDS OF NICKEL WITH OXYGEN.

§ 902. Nickel forms two oxides:

A protoxide composed of.....	
Nickel.....	78.72
Oxygen .....	21.28
	<hr/>
	100.00
and a sesquioxide composed of.....	
Nickel.....	71.13
Oxygen .....	28.87
	<hr/>
	100.00

From this the equivalent of nickel is 29.6, differing by only one decimal from that of cobalt.

*Protoxide of nickel* is obtained in the hydrated state by treating a solution of sulphate of nickel with caustic potassa, when an apple-green precipitate forms, which, when well-washed in boiling water, and then calcined and protected from the air, yields anhydrous oxide as an ash-gray powder. It is also obtained by the calcination of the hydrocarbonate. Although calcined nitrate of nickel leaves some oxide, the temperature must be very high to convert it entirely into protoxide.

*Sesquioxide of nickel* is prepared by subjecting hydrated protoxide suspended in water to the action of chlorine, or treating it

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\* Recognised as a peculiar metal, in 1751, by Cronstedt and Bergmann.

by an alkaline chlorite. This oxide forms a black powder, which dissolves in hydrochloric acid with disengagement of chlorine.

#### SALTS FORMED BY PROTOXIDE OF NICKEL.

§ 903. The hydrated salts of nickel are of a beautiful green colour, the majority of them becoming yellow by losing their water of crystallization, while their solutions are of a beautiful emerald green. From the salts of nickel the fixed alkalies throw down an apple-green gelatinous precipitate, while ammonia does not precipitate highly acid solutions, and gives only a partial precipitation with neutral solutions, as an excess of the reagent redissolves the precipitate, and the liquid turns blue. The carbonates of soda and potassa produce bright-green precipitates of the hydrocarbonate  $\text{NiO}, \text{CO}_2 + \text{NiO}, \text{HO}$ , while the alkaline phosphates and arseniates throw down pale-green precipitates. Prussiate of potash gives a greenish-white precipitate. The acid solutions of salts of nickel are not affected by sulfhydric acid, but are partially precipitated when neutral, especially if the acid of the salt is feeble; while the alkaline sulfhydrates give a black precipitate of hydrated sulphide soluble in an excess of the precipitant.

§ 904. *Sulphate of nickel* is generally obtained from the *nickel-ore*, which is the metallic *speiss* deposited in the bottom of the crucible in the manufacture of *smalt*. It is principally composed of arseniurets of nickel and iron, but frequently contains some traces of cobalt; in which case, the powdered speiss is fused with a small quantity of alkaline glass, to which a little nitre is added, when the oxide of cobalt passes into the vitreous scoriæ, and the purified nickel is concentrated in the lump of arseniuret, because cobalt is more oxidizable than nickel, which has, on the contrary, a greater affinity for arsenic. The arseniuret of nickel is then roasted to drive off the arsenic as completely as possible, and the residue of basic arseniate, after being heated in a crucible with a mixture of carbonate of soda and a small quantity of nitre, is treated with hot water, which dissolves the alkaline salts containing all the arsenic acid in the state of arseniate of soda. The oxide of nickel remaining is dissolved in sulphuric acid, the small quantity of persulphate of iron which the sulphate thus formed always contains being easily removed by boiling the liquid with carbonate of lime, which precipitates only the peroxide of iron, and introduces no foreign salts into the liquid, as sulphate of lime is very slightly soluble.

Sulphate of nickel crystallizes at the ordinary temperature with 7 equiv. of water, but may be obtained combined with 6 equiv. by crystallization from a hot solution.

Crystals of sulphate of nickel with 7 equiv. of water often attain a very large size, and exhibit a remarkable phenomenon of molecular movement: on leaving a large crystal to itself for some days, especially if exposed to solar light, it preserves its outward form,

but loses its transparency; and, if it be then broken, will be found filled with cavities, the walls of which are lined with brilliant crystals of quite another form, and in which the molecules are grouped in a completely different manner, while the substance has not become liquid.

By adding oxalic acid to a solution of sulphate of nickel, no precipitate is immediately formed, while, after some time, a crystalline powder of *oxalate of nickel* is deposited, and only a very small quantity of the metal remains in solution.

#### COMPOUND OF NICKEL WITH SULPHUR.

§ 905. *Sulphide of nickel* is prepared by heating a mixture of oxide of nickel, carbonate of soda, and sulphur, when the sulphide fuses into a bronze-yellow button, if the temperature is sufficiently elevated.

#### COMPOUND OF NICKEL WITH CHLORINE.

§ 906. *Chloride of nickel* is obtained by dissolving the oxide, or metallic nickel, in concentrated chlorohydric acid, when the solution deposits green crystals, which, when heated in a tube protected from the air, part with their water, and yield a volatile anhydrous chloride, which sublimes on the sides of the tube in the form of gold-coloured spangles.

#### COMPOUNDS OF NICKEL WITH ARSENIC.

§ 907. Nickel is found in nature combined with arsenic, in the state of arseniurets,  $\text{NiAs}$  and  $\text{NiAs}_2$  and also occurs as a sulf-arseniuret  $\text{NiS}_2 + \text{NiAs}_2$ . The native arseniurets are sometimes used for the extraction of nickel, but generally the speiss arising from the manufacture of smalt is preferred for that purpose.

#### GERMAN SILVER, ARGENTAN, OR MAILLECHORT.

§ 908. Nickel is technically used for making an alloy capable of a high polish and the lustre of silver. This alloy, which is composed of 100 parts of copper, 60 of zinc, and 10 of nickel, is known in commerce by the various names of *German silver*, *maillechort*, *packfong*, *argentan*. Various ornamental objects are made of it, but it is chiefly used for spurs, for carriage and harness mountings, etc.\* It has been proposed for kitchen utensils, but this use would be dangerous, as the alloy readily oxidizes, particularly when in contact with acid liquids, and produces very poisonous salts.†

\* In England.

† German silver finds much more extensive use in Great Britain and the United States, being now a substance almost universally employed for the manufacture of all articles for useful and ornamental purposes which are to be electro-plated. At Birmingham alone, hundreds of tons are annually fashioned into plate of every description, and subsequently coated with silver or gold by the galvanic process.—*W. L. F.*

## DETERMINATION OF NICKEL, AND ITS SEPARATION FROM THE METALS PREVIOUSLY STUDIED.

§ 909. Nickel is precipitated from its solutions by caustic potassa, or by sulphhydrate of ammonia, and is determined in the state of protoxide, like cobalt, after having been highly calcined; but, as is the case with cobalt, the degree of oxidation of the oxide which remains is uncertain. In exact analyses, it is preferable to reduce the oxide by hydrogen and weigh the nickel in the metallic state.

§ 910. As nickel is separated from the metals previously studied, by the same processes as those described for cobalt, we shall refer the reader to them (898), and proceed to examine only the separation of cobalt and nickel.

Nickel and cobalt are frequently found associated, and their separation, which presents some difficulties, becomes necessary. One of the most simple processes consists in pouring oxalic acid into the solution which contains the two oxides, after which the two oxalates, which precipitated together, are redissolved in ammonia, and the ammoniacal liquid is left in an uncorked bottle, when the ammonia is slowly disengaged, and, as its quantity diminishes, the liquid loses more and more its power of dissolving the oxalates. Now, the two salts not being equally soluble in the ammoniacal liquid, a moment arrives at which the latter does not contain enough ammonia to hold the oxalate of nickel in solution, which is the less easily soluble salt, but at which it can still dissolve the oxalate of cobalt: the oxalate of nickel is then deposited, and the liquid assumes a deeper red tinge. When a bright currant-colour is attained, the liquid is decanted, and then contains only cobalt. The small quantity of cobalt which the precipitate of oxalate of nickel always contains, is separated by again dissolving the oxalate of ammonia, and allowing the liquid to evaporate.

Another process consists in pouring alternately chlorohydric acid and ammonia into the solution which contains the two oxides, until the liquid yields no precipitate with an excess of ammonia, when a sufficient quantity of ammoniacal salt has formed to constitute, with the metallic salts, double salts which are indecomposable by ammonia. The liquid is bottled, and caustic potassa added to it, which does not decompose the double ammoniacal salt of cobalt, while that of nickel parts with the oxide of nickel, which is precipitated. The contact of the air must be avoided during this experiment, as otherwise the cobalt would absorb oxygen and be precipitated in the state of hydrated sesquioxide. The cobalt which remains in the liquid is then precipitated by an alkaline sulphide.

These metals may also be separated very accurately by dissolving them in an excess of chlorohydric acid, and diluting with a large quantity of water, after which the liquid is saturated with chlorine gas, and carbonate of baryta in excess added. The liquid



is then allowed to rest for 18 hours without being heated, when the whole of the cobalt is precipitated as sesquioxide, while the nickel remains in solution. The precipitate, which consists of sesquioxide of cobalt and the excess of carbonate of baryta, is collected on a filter, and, after being well washed with cold water, is dissolved in concentrated chlorohydric acid, after which the baryta is precipitated by sulphuric acid, and then the oxide of cobalt by potassa.\*

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\* Since the author has published the above methods, a still better one has become known, which is the discovery of Liebig and Wöhler, and consists in the following operations:—The two oxides intended to be separated are dissolved in pure cyanide of potassium, and the red solution obtained is boiled to expel the excess of prussic acid; when hydrogen is at the same time evolved, and the cyanide of cobalt changes to cobaltidcyanide of potassium  $\text{Co}_2\text{Cy}_3, 3\text{KC}_y$ , while the nickel remains as potasso-cyanide nickel  $\text{NiCy}_2, 2\text{KC}_y$ . An addition of pure oxide of mercury, suspended in water, then precipitates all the nickel as a mixture of oxide and cyanide, while the mercury replaces the nickel in the double cyanide; after which the precipitate, consisting of oxide and cyanide of nickel, and the excess of oxide of mercury added, is washed and calcined, when pure oxide of nickel remains, and is weighed. The cobalt, which still exists in the solution as cobaltidcyanide of potassium, is then precipitated by protonitrate of mercury, after having neutralized the liquid with nitric acid; when a heavy white precipitate is formed, containing all the cobalt as cobaltidcyanide of mercury, which, by calcination in the air, is converted into pure oxide of cobalt, which is weighed.—*W. L. F.*

## ZINC.

EQUIVALENT = 32.6 (407.5; O = 100).

§ 911. Zinc is now technically employed in a great number of different ways. That found in commerce is not perfectly pure, while the sheet-zinc more nearly approaches perfect purity, because the presence of the smallest quantity of foreign matter considerably diminishes the malleability of the metal and renders it unfit for rolling. Zinc fuses at a temperature of about  $930^{\circ}$ , and boils at a white-heat, when it may be purified by distillation; to effect which, commercial zinc is placed in an earthen retort, which is arranged in a reverberatory furnace, while below the open neck of the retort a vessel containing water is placed to receive the zinc. Another and more suitable apparatus for this distillation consists of a clay crucible A (fig. 521), the bottom of which is perforated,

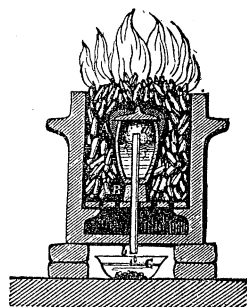


Fig. 521.

and rests on a clay disk, or *cheese* (fromage) B, pierced likewise with a hole. A clay pipe *ab*, the upper end of which reaches the top of the crucible, being hermetically fastened in both apertures, the zinc to be distilled is placed in the crucible, which, after the lid is luted on, is arranged in a furnace so that the pipe may pass through the grate, beneath which is placed a pan C filled with water. When the temperature rises in the furnace, the zinc first fuses, and then boils, when its vapour, descending through the pipe and there condensing, allows the liquid metal to run into the pan. This process is called *distillatio per descensum*.

The distillation of zinc does not free it entirely from the metals with which it is combined, since the very high temperature at which the distillation takes place, causes a small portion of the other metals to be carried over with the vapours of the zinc.

Zinc is of a bluish-white colour, and its fresh fracture exhibits large and very brilliant crystalline laminae. While it is brittle at the ordinary temperature, it becomes malleable at a few degrees above  $212^{\circ}$ , and, when heated to  $392^{\circ}$ , again becomes so brittle that it may be pounded in a mortar. Ignorance of these remarkable properties of zinc for a long time prevented its extensive technical use, and formerly it was only employed for making alloys. It is now rolled into thin sheets for roofing houses, and making bathing-tubs and other vessels of great capacity. Zinc vessels must not be used

for the preparation of food, because the metal readily oxidizes in contact with the air, when in presence of even the weakest acids, and produces poisonous salts.

The density of zinc varies from 6.86 to 7.20, according as the metal has been cast, or rolled.

§ 912. Zinc is a very oxidizable metal, as its surface soon tarnishes by superficial oxidization in a damp atmosphere, while, when heated in contact with the air at a temperature above its melting point, it becomes incandescent and burns with a dazzling white flame, the brilliancy of which is owing to the vapour of zinc, which, by burning in the air, forms oxide of zinc, a perfectly fixed compound, of which the particles, heated to whiteness, communicate a bright lustre to the flame. Zinc dissolves readily in chlorohydric and dilute sulphuric acid, and disengages hydrogen; and the metal, when impure, dissolves more rapidly than perfectly pure zinc. It decomposes aqueous vapour with disengagement of hydrogen, and is converted into an oxide, the reaction commencing at a temperature a little above  $212^{\circ}$ , when the metal exists in a very finely divided state.

Zinc also dissolves with disengagement of hydrogen in a boiling solution of potassa and soda, and forms soluble *alkaline zincates*. When an iron blade is at the same time dipped into the alkaline solution, the water is decomposed even when cold, while the zinc alone dissolves, the iron acting only by producing with the zinc a voltaic current, in which the latter metal becomes the positive element, and thus acquires an affinity for oxygen sufficiently great to decompose water at the ordinary temperature in the presence of potassa. The decomposition of water in the presence of potassa, is effected very remarkably by plates of galvanized iron, when very brilliant small crystals, consisting of a hydrated oxide of zinc  $\text{ZnO} + \text{HO}$  are deposited on the sides of the vessel.

#### COMPOUND OF ZINC WITH OXYGEN.

§ 913. Only one oxide of zinc, a very powerful base, is known, the salts of which are isomorphous with those of magnesia and with the protosalts of iron, cobalt, and nickel. The oxide is obtained by heating the metal in contact with the air until it ignites, when a white flocculent substance, of which a portion is carried off by the current of air, is deposited on the edges of the crucible. The old chemists called it *lana philosophica*, or *pompholix*.<sup>\*</sup> The oxide thus obtained always contains particles of the metal, which it may be freed from by levigation. When pure oxide of zinc is to be prepared, it is better to decompose by heat either nitrate of zinc or the hydrocarbonate which is obtained by adding an alkaline carbonate to the solution of a salt of zinc. When caustic potassa is poured into

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<sup>\*</sup> It also bore the curious name of *nihil album*, "white nothing."

a salt of zinc, a white precipitate of hydrated oxide of zinc is obtained, which retains a certain quantity of alkali with great obstinacy.

Anhydrous oxide of zinc is white, and assumes a yellow shade on the application of heat, which disappears on cooling.

Oxide of zinc is formed of

Zinc.....	81.5
Oxygen.....	18.5
	<hr/> 100.0

whence the equivalent of zinc is 32.6.

Oxide of zinc, when mixed with drying oils, produces a white paint, which may be substituted for white-lead, or ceruse, and has been recently manufactured on a large scale.\* It has the advantage of not being blackened by sulphurous gases, and not exposing the workmen to the same dangerous affections.

#### SALTS FORMED BY OXIDE OF ZINC.

§ 914. The salts of zinc are colourless when the acid is not coloured. Their solutions yield, with potassa, soda, and ammonia, white precipitates which dissolve in an excess of the reagent; and the alkaline carbonates throw down a white precipitate, which also takes place with prussiate of potash and the alkaline phosphates and arseniates. Sulphydric acid does not precipitate the salts of zinc when they contain an excess of acid, but the sulphydrates give white precipitates.

#### *Sulphate of Zinc.*

§ 915. The sulphate, which is the most important of the salts of zinc, is readily prepared in the laboratory by dissolving metallic zinc in dilute sulphuric acid. It crystallizes at the ordinary temperature with 7 equiv. of water, of which 6 are easily driven off by subjecting the salt to a temperature above  $212^{\circ}$ . Crystallized sulphate of zinc dissolves in two or three times its weight of water, at the ordinary temperature, while at  $212^{\circ}$  its solubility may be said to be infinite, as it melts in its water of crystallization.

Sulphate of zinc is prepared on a large scale by roasting blende in heaps, when a portion of the sulphur is disengaged in the state of sulphurous acid, while the greater part of the blende is converted into sulphate of zinc, provided the temperature does not rise above a certain point. The roasted matter is treated with water, and the solution evaporated to crystallization; and in order to render the salt easily transportable, it is generally melted in its water of crystallization, and poured into square moulds of the size

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\* It is extensively manufactured at Vieille Montagne, and also in New Jersey, from the red oxide occurring near Franklin.

of a common brick. The salt is called in commerce *white vitriol*, and is used in the manufacture of calico.

*Carbonate and Hydrocarbonate of Zinc.*

§ 916. When an alkaline carbonate is poured into a solution of sulphate of zinc, a precipitate is obtained, which is not a carbonate, but a hydrocarbonate of zinc ( $2\text{ZnO}, \text{CO}_2 + 3\text{ZnO}, \text{HO}$ ). Anhydrous carbonate of zinc is found in nature, constituting a mineral called *calamine*, which acquires great importance from being the ordinary ore of zinc. Most frequently, calamine exists in compact masses, and more rarely exhibits distinct crystals belonging, like carbonate of lime, to the rhombohedral system.

COMPOUND OF ZINC WITH SULPHUR.

§ 917. Zinc in the state of filings is, when heated with flowers of sulphur, converted into a sulphide; but it is difficult thus to obtain a perfect sulphuration. It is better to heat a very intimate mixture of oxide of zinc and flowers of sulphur, when sulphurous acid is disengaged, and sulphide of zinc  $\text{ZnS}$ , in the form of a yellowish-white powder, remains. Sulphide of zinc is found abundantly in nature, forming a brownish-yellow translucent mineral, crystallized in regular octahedrons, or cubo-octahedrons, and called *blende*.

COMPOUND OF ZINC WITH CHLORINE.

§ 918. Zinc is easily acted on by gaseous chlorine, and converted into a white, butyrous, very fusible substance, which distils only at a red-heat. This chloride is obtained in solution in water, by treating zinc with chlorohydric acid, when the solution, on being evaporated and cooled, becomes crystalline. Chloride of zinc is soluble in water and in alcohol to such an extent, that when an aqueous solution of the salt is concentrated by ebullition, the temperature rises continually to  $482^\circ$ , at which point the chloride becomes anhydrous, but still preserves its liquid state. This property suggests the use of a solution of chloride of zinc instead of oil, for baths in which substances are to be heated to a high but certain temperature.

DETERMINATION OF ZINC, AND ITS SEPARATION FROM THE METALS PREVIOUSLY STUDIED.

§ 919. Zinc is generally precipitated from its solutions by carbonate of soda, after which the liquid is boiled, and the gelatinous precipitate of hydrocarbonate of zinc washed with boiling water, when it is determined in the state of oxide after calcination. If the liquid contains much ammoniacal salt, it must be evaporated to dryness with an excess of carbonate of soda, and then treated with water.

Zinc is frequently precipitated as sulphide by sulfhydrate of ammonia; when the precipitate is washed with water containing a small quantity of the sulfhydrate, in order to prevent the formation of sulphate of zinc by contact with the air. The hydrated sulphide is redissolved in chlorohydric acid, and the zinc precipitated by carbonate of soda as carbonate.

§ 920. In general, zinc is separated from the alkalies and alkaline earths by means of sulfhydrate of ammonia, which precipitates the zinc only as sulphide; but it is more readily separated from baryta by means of sulphuric acid. Lime may also be separated from oxide of zinc by adding to the liquid containing the two bases an excess of ammonia, and some oxalate of ammonia, which precipitates only the lime in the state of oxalate of lime, while the oxide of zinc remains in solution in the excess of ammonia.

The separation of oxide of zinc from magnesia is effected by means of sulfhydrate of ammonia, the precaution being used first to add an ammoniacal salt in sufficient quantity to the liquid to prevent the precipitation of the magnesia by ammonia.

Oxide of zinc is separated from alumina by ammonia in excess, which dissolves the former and precipitates the alumina, while a perfect separation is, however, difficult, as alumina is slightly soluble in ammonia.

Oxide of zinc is separated from oxide of manganese by caustic potassa, which redissolves the former and leaves the oxide of manganese, especially if the liquid is left exposed to the air for some time, so that the protoxide of manganese may be changed into sesquioxide. The separation is, however, rarely effected perfectly, the oxide of manganese always retaining some oxide of zinc; and the precipitate must be redissolved in chlorohydric acid and precipitated anew by an excess of potassa.

In order to separate zinc from iron, the latter metal is first brought to the state of a sesquisalt by means of nitric acid or chlorine, and then ammonia in excess is added, which redissolves the oxide of zinc and precipitates only the hydrated sesquioxide of iron. It is well to redissolve the oxide of iron in an acid and precipitate it a second time by ammonia in excess, as the small quantities of oxide of zinc, which in the first precipitation had been carried down with the sesquioxide of iron, are thus separated.

The separation of zinc from cobalt and nickel is more difficult. The best plan consists in precipitating the metals together by carbonate of soda, and weighing them in the state of oxides after calcination. The mixture of oxides is then placed in a glass globe D (fig. 522), terminating in a curved end *bed*, which descends to the level of a small quantity of water in the bottle E, and a current of dried chlorohydric acid gas is passed through the tube *ab*, while the globe D is heated by an alcohol-lamp. The oxides are thus changed into chlorides, when the chloride of zinc, being very volatile, distils

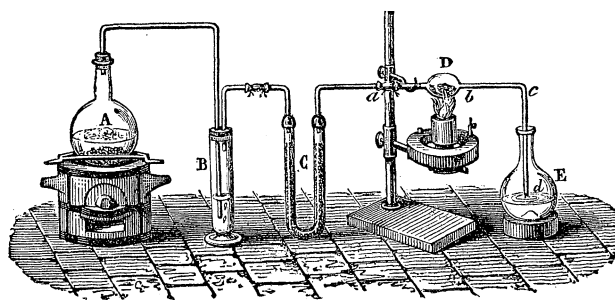


Fig. 522.

over, and condenses in the tube *bcd* and in the water in the bottle. The chlorides of cobalt, or nickel, on the contrary, remain in the globe D. At the close of the operation, the tube *bcd* is detached and thrown into the bottle E, when all the chloride of zinc is dissolved; while, on the other hand, the globe D is heated with acidulated water. The metals, being thus separately dissolved, are precipitated in the ordinary manner.

#### METALLURGY OF ZINC.

§ 921. Calamine is the principal ore of zinc. Silicate of zinc is frequently mixed with calamine, but, as it yields very little metallic zinc, should not be regarded as a true ore. A certain quantity of zinc is extracted from blende. The principal mines of zinc are those of Tarnowitz, in Silesia, Vieille Montagne, near Liège, and several counties in England.

The theory of the metallurgic treatment of calamine is very simple:—The ore is calcined, by which process its carbonic acid is driven off and it is rendered friable, after which it is powdered in mills with edge-stones, and the powder, mixed with charcoal, is heated in earthen retorts in a furnace to a strong white-heat. The oxide of zinc is reduced by the charcoal, while carbonic oxide gas is disengaged, and the metallic zinc condenses in allonges fitted to the retorts.

§ 922. The ore of Vieille Montagne is a mixture of silicate and carbonate of zinc, being sometimes compact and sometimes crystallized. The gangue consists exclusively of clay, in amorphous masses, scattered through the fragments of calamine. The ore is exposed to the air for several months, to allow the clay to rot, after which it is easily separated; while sometimes it is washed, and the clay in this manner almost entirely removed. Two classes of ore are distinguished, according to their aspect and chemical composition, the white ore and red ore, the latter of which contains more iron than the first, and is less rich in zinc, but more

easily worked. The following is the average composition of these two kinds of ore:

		White ore.	Red ore.
Oxide of zinc {	Zinc .....	46.6 .....	33.6
	Oxygen.....	11.7 .....	8.4
Silex and clay.....		14.0 .....	20.0
Water and carbonic acid.....		22.7 .....	20.0
Sesquioxide of iron.....		5.0 .....	18.0
		<u>100.0</u>	<u>100.0</u>

The washed ore is calcined in conical kilns (fig. 523), resembling limekilns, and heated by two lateral furnaces, covered by an arch, and terminating in a canal which opens into the kiln by 20 working-holes *o, o, o*, arranged in 4 or 5 rows, each opening being four inches square. At the lower part of the furnace are two rectangular openings *A*, intended for the removal of the roasted ore, while two cast-iron plates *f, f*, having an inclination of  $45^\circ$ , divide the descending column of ore, and facilitate its escape from the kiln. The

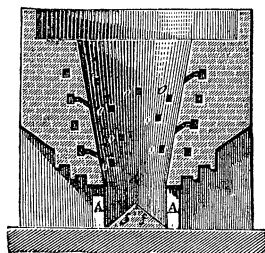


Fig. 523.

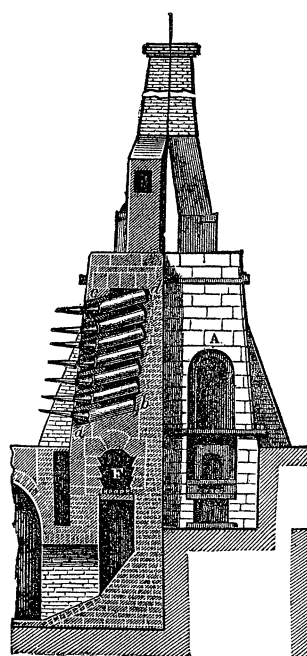


Fig. 524.

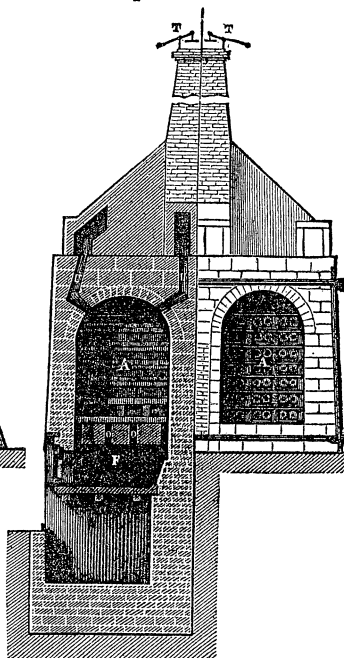


Fig. 525.



calcination is continuous, and the ore is charged from above, the large and small pieces being so mixed as to allow an easy passage for the flame. The ore loses during the calcination its water and carbonic acid; the loss being about 25 per cent. The kilns are heated with pit-coal.

The calcined ore is finely powdered in edge-stone mills, sifted, and then sent to the reducing furnace.

The furnace is composed of four kilns joined together, the shape of each being that of a cylindrical cradle A (figs. 524 and 525), the upper edge of which is about 8.5 feet above the floor. The posterior part of the furnace is made by a wall *bd*, inclined backward, while the anterior part *ac* is, on the contrary, entirely open. The hearth F is below the floor of the furnace, into which the flame enters by 4 holes *o*, *o*, and at the top of the wall are two flues U, U, which open into a chimney in the centre of the building. The chimney, which serves for the 4 kilns, is divided into 4 compartments, each having its own register T. In each furnace 42 retorts of refractory clay are arranged, consisting of long earthen pipes *bd* (fig. 526), closed at one end *d*, 3.4 feet long, with an internal diameter of 5.9 inches. Into each tube a conical cast-iron pipe *cd* (fig. 527) is inserted, which acts as a condenser, and to which is



Fig. 526.



Fig. 527.



Fig. 528.

fitted a second conical sheet-iron pipe *ef* (fig. 528), having at *f* an opening of only 0.8 inch. The earthen pipes are arranged in the kiln in 8 rows above each other, their closed ends resting on 8 projecting edges built in the back wall *bd* of the oven (fig. 524). On the front wall *ac*, which is open, are arranged 8 cast-iron plates, supported by bricks, and intended for the reception of the anterior part of the tubes, which are slightly inclined forward. The kilns are kept burning for 2 months, after which they generally need repairing.

In order to start a new furnace, the open face of the kiln is first closed with brickbats and broken tubes, and cemented with mortar, after which it is heated for several days, at first gradually, and then to a white-heat. After 4 days of preliminary heating, the tubes are introduced by removing the anterior part of the furnace and arranging them after they have been previously heated; the interstices between the tubes and the anterior compartment through which they pass being luted with mortar; and lastly, the conical allonge being adapted to each tube.

When the crucibles are arranged in the furnace, a small quantity of ore and charcoal is first introduced, these charges being successively increased until, after several days, the regular work of the

furnace begins. This period of the operation is that which will alone occupy our attention.

The ore is brought in a wooden box, where it is mixed with charcoal, and a little water added. The charge of a furnace consists of 10 cwt. of calcined calamine, and 5 cwt. of dried pulverized pit-coal, which substances are intimately mixed with an iron shovel. The residue of the preceding distillation is removed from each tube, which then, with its cast-iron receiver, is cleaned by means of an iron rod. The lower tubes are first charged. The mixture is introduced by means of semi-cylindrical sheet-iron shovels (fig. 529), fastened to an iron handle; and when the charging is com-

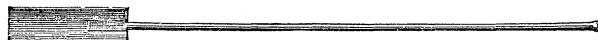


Fig. 529.

pleted the fire is blown up. A large quantity of carbonic oxide is soon disengaged, and burns with a blue flame at the openings of the cast-iron receivers, while in a short time this flame becomes more brilliant, of a greenish-white colour, and evolves white fumes, which is a sign that the distillation of the zinc has commenced, and that it is time to fit the sheet-iron allonges to the tubes. Whatever care may be taken to obtain a uniform temperature, the heat is always greater in some parts of the kiln than in others; for which reason the upper tubes are charged only with the red ore, as being the most easily reduced, while the white is introduced into the lower ones. After 2 hours' firing, the workman detaches the sheet-iron allonges, and shakes them over a sheet-iron receiver, when a dust of zinc and oxide of zinc, called *cadmie*, falls down, which is added to the ore in the succeeding operations. An assistant then holds a large sheet-iron spoon (fig. 530), called a *poëlon*, near the opening of each cast-iron receiver, while the master workman introduces an iron rake, with which he draws out the distilled zinc, which has ac-



Fig. 530.

cumulated in a liquid state at the bottom of the allonge, and in the same way detaches the drops adhering to its sides. The liquid zinc collected in the *poêlons* is covered with metallic scum, consisting chiefly of oxide of zinc, which is carefully removed, and the zinc run into rectangular moulds, in pieces weighing from 60 to 70 lbs. The sheet-iron allonges are immediately replaced and the fire continued. In 2 hours a second drawing is made, and so on until 5 o'clock p. m., when the operation is generally terminated. The tubes are then cleaned, and new ones substituted for those destroyed in the preceding operation. Two operations are thus made in 24 hours, producing together about 6 cwt. of zinc and 30 to 50 lbs. of metallic dust; so that by this treatment, calamine yields about 31 per cent. of zinc, about 10 per cent. remaining in the residue. The metal contained in the residue existed in the state of silicate of zinc, which is not reduced by the charcoal.

The greater part of manufactured zinc being used in the shape of rolled zinc, it is necessary again to melt the ingots, which is done in a reverberatory furnace with an elliptical floor of refractory clay and slightly inclined backward. At the lowest part of the floor is a hemispherical crucible in which the melted zinc collects, and from which it is dipped out and run into moulds of a suitable form for rolling. The plates are being reheated in a second furnace adjoining the first, by means of the hot gases of the former, and, when they have reached a temperature not exceeding  $212^{\circ}$ , are passed between cast-iron rollers. When they are of suitable size, they are cut into rectangular sheets of the dimensions required, the clippings being again fused. Formerly, zinc was fused in large cast-iron pots, which, however, soon became perforated, while the zinc lost many of its qualities by being combined with a small quantity of iron.

§ 923. The furnaces and distilling apparatus used in Silesia differ essentially from those in Belgium. Fig. 531 gives a view of a

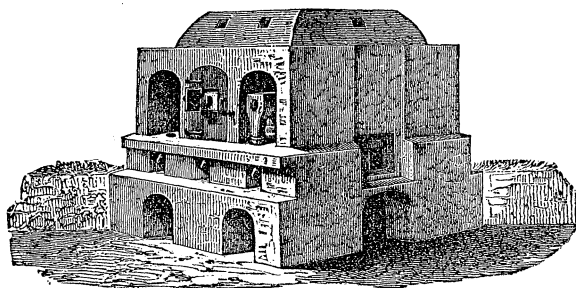


Fig. 531.

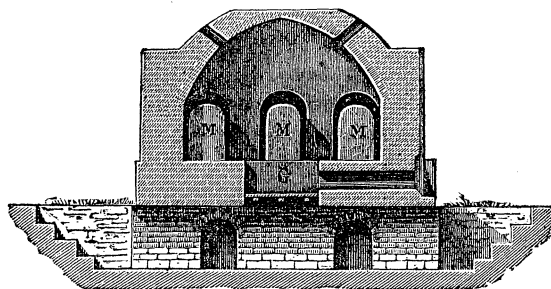


Fig. 532.

Silesian furnace, of which fig. 532 is a vertical section. The distillation is effected in muffles of baked clay M (figs. 533 and 534), about 3 feet in length and 1.5 feet in height, the anterior part of which has 2 openings: the lower opening *a*, through which the residue of distillation is withdrawn, is closed during the operation by a clay

door, tightly luted, while into the upper opening a right angled clay tube *bed*, closed at *d*, is introduced. The ore is charged with a shovel through a hole *c*, which is closed during the distillation

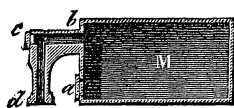


Fig. 533.

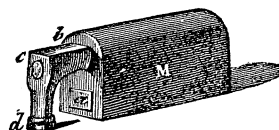


Fig. 534.

with a baked-clay stopper. Six or ten muffles are arranged in two rows in a kiln, the side walls of which have apertures for their passage, which are closed by sheet-iron doors, preventing too sudden a cooling of the allonges *bed*. The kiln is heated with pit-coal burned on the grate *G*, and they are charged with a mixture of equal parts of calcined calamine and charcoal cinders, which, having fallen through the grate, are immediately extinguished in water placed beneath. No pulverized pit-coal is used, lest any coal-dust, carried by the current of gas, should obstruct the allonges; and the calamine itself is reduced to the size of a pea. The zinc runs through the opening *d* of the allonge, and is collected in the spaces *t* of the furnace. Although the operation lasts only 24 hours, the muffles are not emptied until after three operations, when a half-fused greenish mass is extracted as a residue. The calamine is roasted in reverberatory furnaces heated by the waste flame of the reducing furnace. Silesia furnishes the greater portion of the zinc which is brought into commerce.

§ 924. In the Belgian and Silesian processes, the distillation of the zinc is effected *per ascensum*, while the process employed in

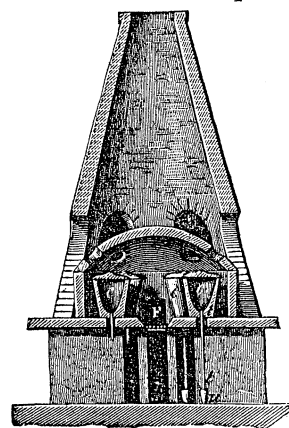


Fig. 535.

England furnishes an example of distillation *per descensum*. The reducing furnaces, resembling very much the ordinary glass-furnace, being circular (fig. 535), and having the hearth *F* in the middle, at a certain distance below the floor of the furnace. The ore, mixed with charcoal, is charged in the crucibles *c*, which are arranged around the hearth, and introduced through several apertures in the arched roof. There is a hole in the bottom of each crucible, into which an iron tube *tt*, passing through an aperture in the floor of the furnace, and opening externally, is introduced. The upper opening of the tube is closed, before the charging, with a wooden stopper, which, by becoming carbonized during the operation, is sufficiently porous

to allow the gaseous zinc to escape, while the ore is still retained; and each pot is covered with a lid accurately luted with clay. The distilled zinc condenses in the iron pipe *tt*, and drops into a sheet-iron receptacle beneath, an iron rod being, from time to time, introduced to detach the zinc which may have become solid, and might ultimately choke the tubes.

§ 925. A certain quantity of zinc is also extracted from blende, which is found in large quantities in several localities, after roasting the blende as perfectly as possible, first in heaps, by which the greater portion of the sulphur is removed and the ore is rendered very friable, and then in a reverberatory furnace, by which the oxidation of the zinc is completed. The roasted ore, which consists of oxide and sulphate of zinc, is reduced by charcoal in a distilling apparatus, in the same manner as calamine.

## CADMIUM.

EQUIVALENT = 56 (700; O = 100).

§ 926. Cadmium\* is a metal still more volatile than zinc: it distils at a red-heat, and the distillation may be effected in glass retorts which are difficult of fusion. In order to obtain pure cadmium, a mixture of oxide or carbonate of cadmium and charcoal is heated in a retort, when the cadmium sublimes and condenses in drops in the neck of the retort. The small drops often crystallize on solidifying, the crystalline form of the metal belonging to the regular system.

Cadmium is a white metal, rather more gray than tin, and possessing a considerable degree of malleability and ductility. Its density is 8.7, and it fuses long before reaching a red-heat. Cadmium does not oxidize appreciably at the ordinary temperature, but on being heated, its vapour ignites and burns with brilliancy. Chlorohydric and dilute sulphuric acid dissolve it with the evolution of hydrogen gas.

## COMPOUND OF CADMIUM WITH OXYGEN.

§ 927. The only oxide of cadmium known is obtained either by heating the metal in the air or by treating it with nitric acid, and then decomposing the nitrate by heat. The oxide forms a brown powder, which resists the highest temperature without volatilizing or melting, and which readily combines with acids, forming colourless salts, unless the acid itself is coloured. Caustic potassa or soda effects a white precipitate with salts of cadmium, consisting of hydrated oxide of cadmium.

Oxide of cadmium is composed of

Cadmium .....	87.5
Oxygen.....	12.5
	<hr/>
	100.0

whence its equivalent is inferred to be 56.

## SALTS FORMED BY OXIDE OF CADMIUM.

§ 928. The salts of cadmium, the greater number of which readily crystallize, are colourless. The fixed alkalies precipitate them from their solutions as gelatinous hydrated oxide, which does not redissolve in an excess of the reagent. Ammonia affords the same

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\* Discovered in 1818, by Hermann and Stromeyer.

precipitate, but an excess of ammonia easily redissolves it. The alkaline carbonates yield a white precipitate of neutral carbonate of cadmium  $\text{CdO}, \text{CO}_2$ , insoluble in an excess of the reagent. Sulphydric acid throws down, even in the presence of a considerable excess of acid, a very beautiful yellow precipitate, while the alkaline sulphhydrates afford the same precipitate, which is insoluble in an excess of sulphhydrate. A blade of zinc, dipped into a solution of a salt of cadmium, precipitates the metal in the form of crystalline spangles.

*Sulphate of cadmium* crystallizes with 4 equiv. of water.

#### COMPOUND OF CADMIUM WITH SULPHUR.

§ 929. *Sulphide of cadmium* is found crystallized in nature, but is a rare mineral. It is obtained artificially by passing a current of sulphydric acid gas through a solution of a salt of cadmium. The beautifully yellow precipitate thrown down is used in painting. Sulphide of cadmium is also prepared in the dry way, by heating oxide of cadmium with sulphur. The sulphide is not attacked by dilute chlorohydric acid, but dissolves in the concentrated acid with the evolution of hydrogen gas.

#### COMPOUND OF CADMIUM WITH CHLORINE.

§ 930. Chloride of cadmium is obtained by heating the metal in a current of chlorine, when a white fusible substance is formed, which sublimes when further heated. By dissolving cadmium in chlorohydric acid, or in aqua regia with an excess of chlorohydric acid, a solution of hydrated chloride is obtained, which crystallizes readily, and loses its water by heat, without being decomposed.

#### DETERMINATION OF CADMIUM, AND ITS SEPARATION FROM THE METALS PREVIOUSLY STUDIED.

§ 931. Cadmium is determined in the state of calcined oxide of cadmium, and, when it exists in solution, is precipitated by carbonate of soda at the boiling point. The precipitation is complete, even when the liquid contains ammoniacal salts.

Cadmium is easily separated from all the metals we have hitherto studied, by passing a current of sulphydric acid gas through the solutions, which must be slightly acidulated by a mineral acid. The precipitate of sulphide of cadmium formed is washed with water containing a small quantity of sulphydric acid, and then redissolved in nitric acid, and the hot solution precipitated by carbonate of soda.

#### EXTRACTION OF CADMIUM.

§ 932. Cadmium occurs in nature as oxide, or carbonate, sparingly scattered through calamine, and is most abundantly found in that of Silesia. When zinc is extracted from this ore, the cadmium

is reduced at the same time, and, as it is much more volatile than zinc, is first disengaged, and burns in the air with the first portions of zinc that are liberated, when a more or less brownish dust is formed, composed of oxide of zinc and 5 or 6 per cent. of oxide of cadmium. This oxide is mixed with  $\frac{1}{4}$  of its weight of charcoal, and then heated to redness in iron tubes, when the greater part of the zinc remains in the residue, because the temperature is not sufficiently high to volatilize it, while the cadmium distils with a portion of the zinc, and condenses in a second sheet-iron tube which acts as a receiver. By subjecting the product to another precisely similar operation, cadmium, containing only a few hundredths of zinc, is obtained. Its purity is ascertained by striking it with a hammer: a very small quantity of zinc deprives it of its malleability. The purification of the metal is completed by dissolving it in chlorohydric acid, and then precipitating it by a blade of zinc.



## TIN.

EQUIVALENT = 58 (725.0; O = 100).

§ 933. Common commercial tin is never absolutely pure, as it always contains small quantities of arsenic and other foreign metals; but Malacca tin is nearly perfectly pure. In order to obtain chemically pure tin, the metal of commerce is treated with nitric acid, which converts it into an insoluble white powder consisting of stannic acid, and which oxidizes foreign substances. The stannic acid is reduced to the metallic state by heating it in a "brasqued" crucible, after being washed with weak chlorohydric acid to remove more certainly the foreign substances.

Tin is a white metal, resembling silver in its appearance and lustre, and possessing a certain characteristic taste and smell, particularly when held for some time between the fingers. It is very malleable, and may be beaten into exceedingly thin sheets, its malleability being greater at 212° than at the ordinary temperature; but its tenacity is very feeble, for a wire of 2 millimetres breaks under a weight of 24 kilogs. On bending a bar of tin a peculiar noise is heard, called the *cry of tin*, which is owing to the internal crystalline texture of the metal. The crystalline particles rub upon each other when the bar is bended, while the latter becomes heated at the point of this internal friction; and if the bending is repeated several times at the same spot, the evolution of heat becomes sensible to the hand.

Tin fuses at 442.4°, giving off at a white-heat appreciable vapours of very feeble tension, for the metal suffers but a slight loss at the temperature of a forge-fire. Tin has a great tendency to crystallization, and its crystalline texture is easily demonstrated by attacking its surface by an acid which removes the outer pellicle.

The surface of the metal then appears to be *watered*, in consequence of the unequal and various reflections of light by the edges of the crystalline laminæ exposed by the acid. Tin may be crystallized by fusion, by melting several pounds of the metal in a vessel, and allowing it to cool slowly over a heated sand-bath. When a solid crust has formed on the surface, it is pierced with a burning coal and the liquid portion evacuated, when quite large crystals of tin, which, however, are rarely well-defined, are often found on the sides of the vessel.

By precipitating tin by means of the galvanic current, it may be obtained in long brilliant prismatic crystals, the form of which has not yet been exactly determined. For this purpose a concentrated solution of protochloride of tin is poured into a glass, and above it

a stratum of fresh water is carefully placed; after which a blade of tin, which traverses both strata, is introduced into the glass, when the blade of tin soon becomes covered with very brilliant metallic crystals.

The density of tin is 7.29, and is not sensibly increased by the hammering of the metal.

Tin is too malleable to be pulverized in a mortar, for which reason tin filings, or the tin-leaf employed to wrap *bonbons* and chocolate, must be taken when the metal is to be used in a finely divided state. Finely divided tin may also be obtained by a peculiar process, consisting in beating the metal, when fused in a capsule, rapidly with a large brush until it is entirely cool, when it is reduced into very small globules, which may be separated into globules of various sizes by a kind of levigation.

Tin does not sensibly change in the air at the ordinary temperature, but at its fusing point becomes quickly covered with a gray pellicle, which is a mixture of protoxide of tin and stannic acid. Oxidation takes place much more rapidly at a higher temperature, and at a white-heat the metal burns with a white flame. Tin decomposes aqueous vapour at a red-heat, and is converted into stannic acid.

Concentrated chlorohydric acid dissolves tin with the disengagement of hydrogen gas. Dilute sulphuric acid also acts on it, when hot, with the evolution of hydrogen, but the metal oxidizes very slowly. Concentrated hot sulphuric acid attacks tin rapidly: sulphurous acid is disengaged, and the metal is changed into protosulphate. Dilute nitric acid oxidizes tin readily and converts it into stannic acid, while the concentrated acid causes a copious evolution of deutoxide of nitrogen. If the acid is very dilute, the tin is converted into stannic acid without disengagement of gas, the water and nitric acid being simultaneously decomposed and nitrate of ammonia formed (§ 122); but when the acid is at its maximum of concentration, that is, in the state of monohydrate  $\text{NO}_5 + \text{HO}$ , it does not attack tin at all, and the metal preserves its brilliancy. But, if a few drops of water be poured into the acid, the reaction takes place with extreme violence, and the liquid is frequently extravasated by the rapid and sudden disengagement of gas.

Aqua regia dissolves tin readily, while, if chlorohydric acid predominates in the mixture, a soluble perchloride of tin is formed.

Tin decomposes water in the presence of the fixed alkalies, and disengages hydrogen when heated with a concentrated solution of potassa or soda, while an alkaline stannate is formed.

#### COMPOUNDS OF TIN WITH OXYGEN.

§ 934. Two well-defined compounds of tin with oxygen are known:

VOL. II.—O

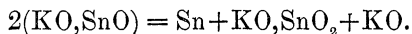
Protoxide of tin  $\text{SnO}$ .

Binoxide of tin  $\text{SnO}_2$ , or stannic acid.

These two oxides can combine with each other and produce several intermediate compounds.

*Protoxide of Tin,  $\text{SnO}$ .*

§ 935. Protoxide of tin is prepared by precipitating a solution of the protochloride  $\text{SnCl}$  by carbonate of ammonia, when carbonic acid is disengaged, and a white precipitate of hydrated protoxide is thrown down. If the liquid be boiled with the precipitate, the latter gives off its water of combination, and is converted into a blackish-gray powder, consisting of anhydrous protoxide, which has great affinity for oxygen, as it oxidizes rapidly in the air, and is converted into stannic acid. The oxide is obtained in a state of greater aggregation, and consequently more fixed, by precipitating protochloride of tin by caustic potassa; when the oxide is first separated in the hydrated state, and combines with the excess of potassa to form a true salt, in which it acts the part of an acid. But, by boiling the liquid, this combination is destroyed, and the oxide is precipitated in the anhydrous state, in the form of small black crystals, which, after being washed and dried in the air, remain unchanged for any length of time. When this substance is heated in an oil-bath to about  $482^\circ$ , it suddenly decrepitates, increases considerably in volume, and is converted into a number of small brown laminæ, which are soft to the touch. The oxide has not changed in weight during the transformation, and has only passed into an isomeric modification; so that this phenomenon must be attributed to a molecular movement, caused, probably, by a change in the crystalline system. The brown modification of protoxide of tin is immediately obtained by precipitating a solution of protochloride of tin by an excess of ammonia, and boiling the liquid, when it is evaporated in vacuo. The solution of the protoxide in potassa deposits black crystals of the first modification of the oxide; while if, on the contrary, a solution of the protoxide of tin in potassa be highly concentrated by rapid boiling, the oxide is decomposed into metallic tin which is separated, and stannic acid which remains combined with the potassa:



Lastly, protoxide of tin may be obtained in the form of a red powder, by decomposing the protochloride by ammonia, boiling the liquid a few moments, and then evaporating it at a gentle heat; the protoxide of tin is converted into small grains of a beautiful red colour, under the influence of the sal-ammoniac formed during the reaction. The red oxide is changed into the brown modification by simple friction with a hard body.

Protoxide of tin ignites like tinder when heated in contact with the air, and is changed into stannic acid.

Protoxide of tin is composed of

Tin.....	87.88
Oxygen.....	12.12
	<hr/> 100.00

The equivalent of tin is therefore 58.

*Stannic Acid*  $\text{SnO}_2$ .

§ 936. Stannic acid may be obtained under two isomeric modifications, which are clearly distinguished from each other by chemical properties. The first modification, called *metastannic acid*, is the white powder obtained by treating tin by nitric acid; while the second, to which the name of *stannic acid* is given, is prepared by decomposing perchloride of tin  $\text{SnCl}_4$ , by water, or a soluble stannate by an acid.

*Metastannic acid* is found crystallized in nature in some of the old rocks, forming very beautiful, brilliant crystals, generally of a deep brown colour, and yielding a yellowish powder. The same substance is obtained by oxidizing tin by nitric acid, when a white powder, which is a hydrate, is formed, but which changes by calcination into anhydrous metastannic acid. Hydrated metastannic acid, such as is formed by the action of nitric acid on metallic tin, has, when dried in the air, the formula  $\text{SnO}_2 + 2\text{HO}$ . It loses one-half of its water at  $212^\circ$ , and then presents the composition  $\text{SnO}_2 + \text{HO}$ , while it loses all its water at a higher temperature.

Metastannic acid is not decomposed by heat alone, but is readily converted into metallic tin by contact with charcoal and the combustible gases. It is insoluble in water and in dilute nitric and sulphuric acid, while concentrated sulphuric acid dissolves it in considerable proportions. The compound formed is not destroyed by adding water to the liquid; but by boiling, the metastannic acid separates in the state of hydrate  $\text{SnO}_2 + 2\text{HO}$ . Chlorohydric acid dissolves it, and transforms it into perchloride of tin  $\text{SnCl}_4$ .

Metastannic acid forms crystallizable salts with the alkalies. It dissolves readily, when cold, in a solution of potassa, and, if fragments of potassa be added to the liquid, its solvent power is so far weakened as to cause the metastannate of potassa to be deposited in the form of a crystalline crust, which is separated and spread on a plate of unglazed porcelain, when the mother liquid which moistens them is thus absorbed. Analysis has proved the formula of this salt to be  $\text{KO}, 5\text{SnO}_2 + 4\text{HO}$ ; and as that of the metastannate of soda is similar, the conclusion follows that the equivalent of stannic acid which combines with 1 equiv. of the base is not  $\text{SnO}_2$ , but rather  $\text{Sn}_2\text{O}_3$ . Metastannate of potassa dissolves in water without change, and the liquid leaves after evaporation a gummy,

uncrystalline residue. Heating to redness destroys the compound, and the metastannic acid becomes anhydrous and insoluble, so that water will only remove pure potassa. An acid, poured into a solution of an alkaline metastannate, precipitates the metastannic acid in the form of a gelatinous substance, which appears to contain more water than the hydrate  $\text{Sn}_5\text{O}_{10} + 10\text{HO}$ , and which is soluble in ammonia, while the hydrate  $\text{Sn}_5\text{O}_{10} + 10\text{HO}$  is not. A slight elevation of temperature, inferior even to that of boiling water, causes the gelatinous acid to pass into the state of the hydrate, which is insoluble in ammonia.

*Stannic acid* is obtained by decomposing perchloride of tin by ammonia, or a soluble stannate by an acid. It is a white gelatinous precipitate, insoluble in water, but readily dissolving in dilute nitric and sulphuric acid, while metastannic acid is insoluble under the same circumstances. The formula of stannic acid, dried in vacuo, is  $\text{SnO}_2 \cdot \text{HO}$ . A slight elevation of temperature causes it to pass into the metastannic modification, even without losing its water.

Stannic acid dissolves readily in alkaline solutions, and the liquid, when evaporated in vacuo, yields beautiful colourless and transparent crystals, of the formula  $\text{KO}, \text{SnO}_2 + 4\text{HO}$ . It will hence be seen that stannic acid saturates four times as much base as metastannic acid. The same salt is obtained by heating metastannic acid with an excess of potassa in a silver crucible, when the metastannic is converted into stannic acid. The completeness of the transformation may easily be ascertained by dissolving a small quantity of the substance in water, and adding an excess of nitric acid; when the stannic acid, which at first is precipitated, is redissolved in the acid liquid, which would not take place if metastannic acid were still present. Stannate of potassa is not decomposed by heat like the metastannic, but loses its water, while it redissolves in water without change.

§ 937. Several oxides of tin, intermediate between the protoxide and stannic acid, are known. By digesting hydrated metastannic acid with a concentrated solution of protochloride of tin, the liquid becomes strongly acid, and the metastannic acid is converted into a yellowish powder, which may be considered as a compound of metastannic acid and protoxide of tin, having the formula  $\text{SnO}, \text{Sn}_5\text{O}_{10} + 4\text{HO}$ . Another intermediate oxide of tin is obtained by mixing hydrated sesquioxide of iron with a solution of protochloride of tin, when a yellowish precipitate is formed, which may be considered as a stannate of tin  $\text{SnO}, \text{SnO}_2$ .

#### PROTOSALTS OF TIN.

§ 938. Only a small number of salts formed by protoxide of tin is known. The protosulphate is obtained by saturating, when hot, dilute sulphuric acid with recently prepared and moist hy-

drated protoxide of tin. The oxide is dissolved, and, on cooling, small crystalline lamellæ of protosulphate of tin  $\text{SnO}, \text{SO}_3$  are deposited. This salt readily dissolves without change in cold water, while heat decomposes it in its solution, and precipitates a subsulphate. Protosulphate of tin forms with the alkaline sulphates double sulphates, which are more fixed than the simple sulphate of tin, and may be obtained crystallized.

*Protonitrate of tin* is prepared by dissolving hydrated protoxide in weak nitric acid, when the salt remains in solution; but it is decomposed when the liquid is evaporated, while stannic acid is formed.

#### SALTS FORMED BY STANNIC AND METASTANNIC ACID ACTING THE PART OF A BASE.

§ 939. It has been shown that metastannic acid combines with concentrated acids, and that stannic acid dissolves even in dilute acids. True salts, in which these bodies act the part of bases, are thus formed; but they have been too little studied to require our further consideration.

#### COMPOUNDS OF TIN WITH SULPHUR.

§ 940. Tin forms two compounds with sulphur: a protosulphide  $\text{SnS}$  corresponding to the protoxide, and a bisulphide  $\text{SnS}_2$  corresponding to stannic acid.

*Protosulphide of tin* is prepared by heating a mixture of tin filings and sulphur to redness in an earthen crucible, pulverizing the product of this first operation and reheating it with an additional quantity of sulphur, when a mass of a deep gray colour, with very brilliant large crystalline lamellæ, is obtained. The same sulphide is precipitated as a deep brown, nearly black powder, in a hydrated state, when a current of sulphydric acid gas is passed through a solution of protochloride of tin. Concentrated chlorohydric acid dissolves protosulphide of tin with the disengagement of sulphydric acid, while the presence of a small excess of the former, in a dilute solution of tin, does not prevent the salt from being completely precipitated by sulphydric acid.

Perchloride of tin  $\text{SnCl}_2$  yields with sulphydric acid a yellow precipitate of hydrated *bisulphide of tin*  $\text{SnS}_2$ . If sulphydric acid gas and vapour of anhydrous perchloride of tin be passed through a tube heated to a dull red, bisulphide of tin is deposited in the form of very brilliant crystalline lamellæ, of a beautiful golden-yellow colour, which substance is technically prepared in the dry way, and is used, under the name of *mosaic gold*, for bronzing wood. This product is obtained as follows:—An amalgam of 12 parts of tin and 6 parts of mercury, pulverized in a mortar, is mixed with 7 parts of flowers of sulphur and 6 parts of sal-ammoniac, and heated in a long-necked matrass in a sand-bath, the tem-

perature of which is gradually raised to a dull red. Sulphur, sal-ammoniac, sulphide of mercury, and protochloride of tin condense in the globe and in the neck of the matrass, while mosaic gold remains at the bottom in the form of a very light, gilded mass, formed by the union of a large quantity of small crystalline lamellæ. The theory of this operation is quite complicated: finely divided tin, when heated with sulphur at a low temperature, is changed into an amorphous bisulphide, which does not present the gilded spangles which alone give it a technical value. By being still further heated it parts with one-half of its sulphur, and passes into the state of monosulphide, which the sal-ammoniac added to the mixture prevents, because, by becoming volatile below a dull red-heat, it absorbs a considerable quantity of latent caloric; but it facilitates at the same time the sublimation, and, consequently, the crystallization of the mosaic gold which is carried over by the vapour.

#### COMPOUNDS OF TIN WITH ARSENIC.

§ 941. Tin and arsenic combine readily, and in all proportions, forming very brittle crystalline compounds. The arseniurets of tin disengage mixtures of pure hydrogen and arseniuretted hydrogen by treatment with chlorohydric acid.

#### COMPOUNDS OF TIN WITH CHLORINE.

§ 942. Tin forms two compounds with chlorine: a protochloride  $\text{SnCl}$ , corresponding to the protoxide, and a bichloride  $\text{SnCl}_2$ , corresponding to stannic acid.

*Protochloride of tin* is obtained by dissolving tin in concentrated boiling chlorohydric acid, when hydrogen gas is evolved. This salt is used in dyeing, and is prepared on a large scale by heating curved bars of tin in large retorts with concentrated chlorohydric acid, after which the saturated liquid is decanted, and the protochloride of tin separated by evaporation in the form of hydrated crystals, of the formula  $\text{SnCl} \cdot 2\text{H}_2\text{O}$ .

Protochloride of tin dissolves without alteration in a small quantity of water, while a large quantity of this liquid decomposes it, and precipitates an insoluble oxychloride  $\text{SnCl} + \text{SnO}$ .

Crystallized protochloride of tin can be freed from its water by heating in a retort, while a small quantity of the chloride is always decomposed during this desiccation, and chlorohydric acid is disengaged; but if the temperature be raised to redness, the protochloride distils over unaltered. Protochloride of tin combines readily with the alkaline chlorides, and yields easily crystallizable double chlorides.

Protochloride of tin has such an affinity for oxygen that it readily absorbs this gas from the air, and abstracts it from a great number of oxides, which it reduces to an inferior degree of oxidation, or

even to the metallic state. It readily precipitates mercury, gold, and silver from their solutions in the metallic state, and reduces the salts of sesquioxide of iron and protoxide of copper  $\text{CuO}$  to the minimum of oxidation.

§ 943. *Perchloride of tin* is readily obtained by treating tin by an excess of chlorine. The affinity of these two bodies is so great that tin filings ignite when thrown into a bottle filled with dry chlorine. In order to prepare any quantity of perchloride, some tin is placed in a tubulated glass retort, furnished with a well-cooled receiver, and a current of chlorine is passed through the tubulure, when the tin immediately combines with the chlorine; and, if the retort be gently heated, a liquid distils over and condenses in the receiver. This liquid, which is generally tinged with yellow by the chlorine it contains in solution, is purified by shaking it with tin filings or protochloride of tin and redistilling it. This substance may also be prepared by heating, in a glass retort, a mixture of 1 part of tin filings and 5 parts of chloride of mercury or corrosive sublimate.

Perchloride of tin forms a colourless liquid of the specific gravity 2.28, and which boils at  $248^{\circ}$ , the density of its vapour being 9.2. It gives off very thick white fumes when in contact with the air, owing to the immediate combination of the vapour of the anhydrous chloride, the tension of which is very high at the ordinary temperature, with the aqueous vapour contained in the atmosphere, and the resulting formation of a hydrate which has no sensible tension, and is, consequently, precipitated. If a few drops of water be added to the anhydrous perchloride, a noise resembling that produced by plunging a red-hot iron in water is heard, and the perchloride then combines with the water with great evolution of heat, giving rise to a hydrated chloride of the formula  $\text{SnCl}_2 + 5\text{H}_2\text{O}$ , which is deposited in beautiful crystals.

The same hydrated perchloride of tin may be obtained by dissolving tin in aqua regia containing an excess of chlorohydric acid, or by passing chlorine through a solution of protochloride of tin. The hydrated perchloride dissolves in a small quantity of water, and in any quantity whatever of this liquid when it is sufficiently acidulated with chlorohydric acid, while an addition of a quantity of fresh water again decomposes it, and causes the precipitation of hydrated stannic acid.

Hydrated perchloride of tin is decomposed by heat, when chlorohydric acid is disengaged and metastannic acid remains. Heated with anhydrous phosphoric acid, or with concentrated sulphuric acid, it imparts its water to them, and the anhydrous perchloride distils over.

The anhydrous perchloride of tin was called by the old chemists the *fuming liquid of Libavius*.



Perchloride of tin combines with a great number of metallic chlorides, forming readily crystallizable double chlorides, which all consist of 1 equiv. of perchloride of tin and 1 equiv. of the other metallic chloride. The anhydrous perchloride combines with sulphydric acid, and also forms with phosphuretted hydrogen gas a compound of the formula  $\text{PH}_3, \text{SnCl}_2$ .

#### DISTINCTIVE CHARACTERS OF THE SOLUBLE COMPOUNDS OF TIN.

§ 944. Tin forms two series of soluble compounds: 1st, those which correspond to the protoxide  $\text{SnO}$ , such as the protochloride and the soluble salts formed by the protoxide; and 2dly, compounds corresponding to stannic acid; that is, perchloride of tin and the soluble compounds of stannic acid with the acids. These two series present different reactions, which it is necessary to examine separately.

#### *Characters of the Protosalts of Tin.*

§ 945. The salts of the protoxide of tin are free from colour when the acid is itself colourless, and always strongly redden tincture of litmus. A small quantity of water in most cases dissolves them, while a greater quantity of this liquid decomposes them, forming a white precipitate, which is generally a basic salt. This precipitation is avoided by acidulating the water with a certain quantity of chlorohydric acid.

The caustic alkalis throw down a white precipitate, which is soluble in an excess of the reagent, while, by boiling the liquid, anhydrous protoxide of tin separates in the form of a black powder. Ammonia also throws down a white precipitate, which is, however, insoluble in an excess of ammonia.

The alkaline carbonates likewise yield white precipitates, which are insoluble in an excess of the reagent, and become black by boiling the liquid.

Sulphydric acid precipitates them as a deep-brown powder, while the alkaline sulphhydrates throw down a dirty-white precipitate, which dissolves in a great excess of the reagent.

Prussiate of potash yield a white precipitate.

Salts of mercury are reduced by the protosalts of tin, a gray precipitate of very finely divided metallic mercury being formed, which collects in globules by trituration.

Chloride of gold gives a precipitate which is purple when the solutions of protoxide of tin are very dilute, and brown when they are more concentrated.

A blade of iron or zinc precipitates tin in the form of gray crystalline spangles, which assume under the burnisher the ordinary colour and lustre of tin.

*Characters of the Soluble Compounds of Tin, corresponding to Stannic Acid.*

§ 946. The characters about to be indicated all refer to the perchloride, which is the only soluble compound corresponding to stannic acid which has been properly studied.

A solution of perchloride of tin always has a strong acid reaction, and is decomposed by a large quantity of water, affording a white precipitate of hydrated stannic acid.

Potassa, soda, and ammonia yield a white precipitate, which dissolves in an excess of the reagent; but the liquid does not throw down a black precipitate on being boiled, as is the case with the compounds of the protoxide.

The alkaline carbonates disengage carbonic acid, and give a white precipitate, which is neither soluble in an excess of the reagent nor turns black by ebullition.

Prussiate of potash gives a white precipitate, which does not form until after some time.

Sulphydric acid gives a dirty-yellow precipitate, which also does not appear immediately, and which, when formed by alkaline sulphhydrates, is soluble in an excess of the reagent.

Chloride of gold throws down no precipitate from a solution of perchloride of tin, which reaction clearly distinguishes the perchloride from the compounds of the protoxide of the metal. Perchloride of tin does not precipitate mercury from its solutions in the metallic state.

Iron and zinc precipitate metallic tin.

DETERMINATION OF TIN, AND ITS SEPARATION FROM THE METALS PREVIOUSLY STUDIED.

§ 947. Tin is always determined in the state of calcined stannic acid. Sometimes it is precipitated as sulphide, which is converted into stannic acid by roasting in a platinum crucible; taking care to add a few drops of nitric acid before the calcination, in order to prevent the separation of metallic tin, which would soon attack the crucible. After the roasting, the crucible is allowed to cool, a small quantity of carbonate of ammonia added, and it is again heated to drive off more readily the last traces of sulphuric acid.

Tin is easily separated from all the metals which we have hitherto studied, except from cadmium, by means of sulphhydric acid. The substances are dissolved in chlorohydric acid, so that the tin may exist in the state of a protochloride, and a current of sulphhydric acid is passed through the liquid, in which a large excess of chlorohydric acid is left. When the liquid contains an excess of sulphhydric acid, the bottle is loosely corked, and left to stand for several hours at a temperature of from 120° to 140°. The precipitate is

then collected on a filter, and, if it is composed only of sulphide of tin, is converted into stannic acid by means of nitric acid.

If the substance contains tin and cadmium, these metals are precipitated together by sulphydric acid, and the two sulphurets are treated with nitric acid, which converts the tin into insoluble stannic acid, and dissolves the cadmium, which is then precipitated from its solution by the processes indicated in § 931.

#### METALLURGY OF TIN.

§ 948. The binoxide, which is the only tin-ore, originally occurs only in the oldest rocks, forming small veins, or irregular threads, in the granitic formations; but it is sometimes also found in the disaggregated sands arising from the destruction of these rocks. The principal localities of tin are in Saxony, Bohemia, in Cornwall in England, and in the East Indies. The sands containing tin found in Brittany are too poor to be worked with advantage. The crushed stanniferous rocks and the stanniferous sands are washed, in order to separate the gangue mechanically, which is an easy operation, as the oxide of tin is much heavier than the gangue, and, as it is very hard, yields but little dust under the stamper. Sands containing only  $\frac{1}{2}$  per cent. of tin may yet be advantageously concentrated by washing.

The washed ores, which consist of a mixture of oxide of tin and some very heavy metalliferous minerals, such as the crystallized sulphides, sulfarseniurets, and oxides of iron, etc., are roasted in heaps or in kilns, when the oxide of tin remains unaltered, while the sulphides and sulfarseniurets become partially oxidized and disaggregated, so that if the ore be again subjected to the stampers, the roasted substances are pulverized, while the oxide of tin remains nearly in its original condition. By another washing the roasted and stamped sand is easily freed from the substances which have been altered by roasting, and a very rich ore is obtained, yielding often more than 50 per cent. of metallic tin.

In Saxony, the ore is fused in a cupola-furnace of about 9 feet in height (figs. 536 and 537). The sides of the oven A are made of slabs of granite, while the bottom consists of a single stone D, called the *sole-stone*, which is properly hewn, and rapidly inclines toward the anterior part of the furnace, called the *breast*. The fused materials constantly run into an exterior crucible B, made of slabs of granite lined with damp charcoal. At the lower part of this furnace is a hole which opens over a cast-iron pot C.

The furnace is charged by alternate layers of ore and charcoal, the combustion being fed by a blowing-machine, the nozzle of which passes through the twyer *o*.

The oxide of tin is reduced by the carbonic oxide which is produced by its contact with the fuel. The gangue itself, being generally very fusible, yields a doughy scoriæ, which flows with the tin

into the basin B, whence it

Fig. 536.

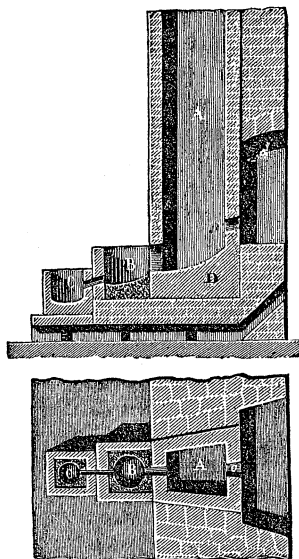


Fig. 537.

is removed from time to time. When the basin B is filled with melted metal, the stopper is removed from the hole, and the metal runs into the cast-iron pot C, where it is stirred with a stick of green wood,\* which, by being partially carbonized in the hot liquid, causes a bubbling, produced by the disengagement of gas, which raises the dross which is scattered through the metal to the surface of the bath, while it, at the same time, reduces the oxide of tin beneath to the metallic state. When the temperature of the metal is only a few degrees above that of its fusion, it is allowed to rest, and is then removed with iron ladles and run into moulds. The upper strata furnish the purest metal, while those at the bottom contain the greater portion of foreign substances.

As the scorïæ do not become perfectly fluid, they always contain a quantity of grains of tin, for which reason the richest are added to the ore and fused with the next charge, while the poorest are stamped and the metallic grains separated by washing. The greater part of the scorïæ is, however, smelted separately in the same furnace, by increasing the blast and quantity of fuel, by which more fluid scorïæ are obtained, from which the tin separates more readily, but is gained only in inferior quality.

§ 949. In England, the ore of the stanniferous sands is treated nearly in the same manner, the furnaces being only much higher. The tin furnished by the upper strata of the crucible is alone run into bars, while the balance is again melted. The bars of tin are sometimes heated to above  $212^{\circ}$  and allowed to fall from a certain height, when the metal, which is very brittle at this temperature, breaks into small crystalline fragments, and is then called *grain-tin*.

The ore taken from the veins is much less pure than that of the sands. After the primary stamping and washing, it is roasted in a reverberatory furnace, when sulphates of iron and copper are formed, which are washed out and separated by crystallization. The ore is then again washed, and the sludge arising from it is

\* This process, which is called *poling*, is effected in the Cornish tin-works by boiling billets of green wood in the melted tin, where they are kept under the surface by means of an iron frame.—W. L. F.

heated on the hearth of a reverberatory furnace with powdered charcoal, to which lime is added to hasten the fusion of the gangue. The scorix are ladled out from time to time, and the tin is run into moulds.

The tin obtained by this process is refined by heating the metal slowly on the hearth of a reverberatory furnace, when the pure tin melts first, and runs out of the furnace, as the hearth is inclined toward the tap-hole, leaving on the hearth an alloy of tin with foreign substances. This method of refining is called *liquation*. Frequently, two successive liquations are necessary in order to obtain very pure tin.

§ 950. Tin is used in the manufacture of various articles, such as kitchen utensils, cotton machinery, etc., etc.; a small quantity of lead being often added to it to render it less brittle. The alloy generally employed contains 18 per cent. of lead.

Tin is also made in very thin sheets, called *tin foil*, and used either for tinning glass or for wrapping *bonbons*, chocolate, etc. Tin foil is manufactured by beating, only the best tin being used. It is first run into plates, which are hammered until their thickness is reduced to about 1 millimetre, after which 8 or 10 plates are laid on each other, and the hammering continued until they are sufficiently thin, when they are cut in half, and again laid on each other and beaten, which process is repeated until a hundred sheets, of the thickness required, are obtained.

One of the most important applications of tin is that of tinning sheet-iron, as was fully described in § 847.

## TITANIUM.

EQUIVALENT = 25 (312.5; O = 100).

§ 951. Titanium\* has been found combined with oxygen in several minerals: *rutile* is nearly pure titanic acid, and *titanic iron* is a mixture, or a compound of titanic acid and oxide of iron. Certain iron-ores contain a very small quantity of these titanic minerals; and metallic titanium† is often found in the products of the blast-furnaces in which such ores are smelted. It is especially met with in the metallic masses which adhere to the sides of the furnace, toward the close of the blast, when this process is beginning to slacken, and then appears under the form of small, very brilliant cubic crystals of a copper-red colour, scattered through a mass of half-refined metal, slag, and frequently sulphide of iron. These masses are treated with chlorohydric acid, which dissolves the iron and does not attack the titanium; by which a large portion of the little crystals are detached, while they still remain mixed with particles of slag, from which they are easily separated by levigation, their density being 5.3, while that of the slag is much lower. These crystals are hard enough to scratch quartz, and are unaffected by concentrated acids, except by aqua regia, which, however, requires a long time to act on them.

When titanic acid is heated in a forge-fire in a "brasqued" crucible, it is converted into an aggregated black mass, which is an inferior oxide of titanium, while the portions in immediate contact with the charcoal are still more reduced, having passed into the state of metallic titanium, which forms a pellicle of a copper-red colour around the mass.

The best method of preparing metallic titanium in the laboratory consists in decomposing by heat perchloride of titanium, which is a volatile liquid, in a retort of hard glass placed in a furnace, and through which a current of dry ammoniacal gas is passed; when the ammonia immediately combines with the perchloride of titanium, which is converted into a white powder. The retort is then surrounded by burning coals and the current of ammoniacal gas kept up; when a large quantity of sal-ammoniac is sublimed and condensed on the globe and in the neck of the retort, the metallic titanium remaining at the bottom in the form of very bril-

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\* Discovered in 1791, by W. Grégor.

† This product is not metallic titanium, as was erroneously supposed, but a combination of nituret and cyanide of titanium, according to the formula  $\text{Ti}_2\text{C}_2\text{N} + 3\text{Ti}_2\text{N}$ .—W. L. F.

VOL. II.—P

liant small spangles of a purple-red colour. The retort is allowed to cool, still maintaining the gaseous current, and the titanium is then removed.

The titanium thus prepared is more easily attacked by acids than that of the blast-furnaces, and nitric acid readily converts it into titanic acid. Heated in the air it becomes incandescent, and is changed into a white powder of titanic acid.

#### COMPOUNDS OF TITANIUM WITH OXYGEN.

§ 952. Three compounds of titanium with oxygen are known :

A protoxide  $\text{TiO}$ .

A sesquioxide  $\text{Ti}_2\text{O}_3$ .

Titanic acid  $\text{TiO}_2$ .

Titanic acid, which is the most important compound, occurs in nature in the form of brownish-yellow opaque crystals, called *rutile* by mineralogists. Rutile, which is not pure titanic acid, but generally contains one or two hundredths of oxide of iron, is isomorphous with native binoxide of tin. Other minerals, formed by sesquioxide of titanium combined with protoxide of iron, and called *titanic irons*, appear to be analogous to magnetic oxide of iron. Lastly, the mineral, called *anatase*, which forms crystals of a beautiful blue colour, is composed of nearly pure titanic acid. Rutile is attacked neither by acids nor alkaline solutions, but is acted on, at a red-heat, by the alkalies and alkaline carbonates. Titanic acid may be obtained in a gelatinous state, in which it combines with the acids by heating finely powdered rutile with two or three times its weight of chloride of barium in a strong forge-fire. The powdered substance is calcined and treated with hot water, to dissolve the chloride of barium which has been left unchanged, when the residue is composed of titanate of baryta and oxide of iron. It is heated in a porcelain saucer with concentrated sulphuric acid, and the temperature elevated sufficiently to drive off the greater part of the excess of sulphuric acid ; after which it is again treated with water, when a residue of sulphate of baryta remains, which is separated by filtering. An excess of ammonia added to the liquid, which contains sulphates of titanium and iron dissolved in an excess of sulphuric acid, precipitates the titanic acid and oxide of iron, after which a small quantity of sulphhydric acid is passed through to convert the oxide of iron into a sulphide. When the gelatinous precipitate has become black, a portion of the supernatant liquid is decanted and replaced by a solution of sulphurous acid, which dissolves the sulphide of iron by transforming it into a hyposulphite. When the precipitate is completely discoloured, it is collected on a filter and washed with boiling water.

Gelatinous titanic acid dissolves in the acids, and by boiling its dilute solutions the greater part of the titanic acid is again depo-

sited. When subjected to heat, a moment arrives at which the substance suddenly becomes incandescent, remaining so only for a moment, after which the titanic acid becomes insoluble in acids. Titanic acid forms no crystallized compounds with the acids, while it forms substances which assume a crystalline texture on cooling by fusion with potassa or soda. But these substances are decomposed by treatment with water, and while an insoluble residue of titanate with a large excess of acid remains, the alkaline liquid contains but little titanic acid.

Titanic acid, heated in a forge-fire in a brasqued crucible, is converted into a black substance, which some chemists regard as a *protoxide*  $\text{TiO}$ , but the existence of this substance is not sufficiently proved.

By heating it to a high temperature in a current of hydrogen gas, the titanic acid is converted into a black powder, the composition of which very nearly approaches that of the oxide  $\text{Ti}_2\text{O}_3$ . The existence of a *sesquioxide of titanium* is, moreover, placed beyond doubt by that of the sesquichloride  $\text{Ti}_2\text{Cl}_3$ , from which it may be obtained. In fact, on adding ammonia to a solution of sesquichloride of titanium, a brown precipitate of hydrated sesquioxide is obtained, which, on being left to itself in water, becomes first black, and then blue, and at last is converted into white titanic acid, with the evolution of hydrogen gas. By treating sesquichloride of titanium with sulphuric acid, a *sesquisulphate of titanium*, which crystallizes with difficulty, is obtained.

#### COMPOUNDS OF TITANIUM WITH CHLORINE.

§ 953. Two chlorides of titanium are known: a sesquichloride  $\text{Ti}_2\text{Cl}_3$ , and a bichloride  $\text{TiCl}_2$ , corresponding to titanic acid  $\text{TiO}_2$ .

*Bichloride of titanium* is prepared by decomposing an intimate mixture of titanic acid and charcoal, heated to a strong red-heat, by dry chlorine, for which purpose the apparatus described for the preparation of chloride of silicium (§ 245), and represented in fig. 538, is used.

A mixture of charcoal and rutile, reduced to an impalpable powder, is made into a consistent paste with a certain quantity of oil, and calcined to redness in an earthen crucible in the shape of small balls. The balls, which preserve their form, and consist of an intimate and porous mixture of titanic acid and charcoal, are introduced into an earthen retort C, into the tubulure  $\alpha$  of which a porcelain tube  $ab$  is introduced, descending to the bottom of the retort. After placing the retort in a furnace and fitting a condensing apparatus to its neck, a current of dry chlorine is passed through the tubulure  $ab$ ; and, when the apparatus has become filled with the gas, the retort is heated to a strong red-heat, while the current of chlorine is continued; when the bichloride of titanium condenses in the refrigerating apparatus, and may be obtained in large quan-



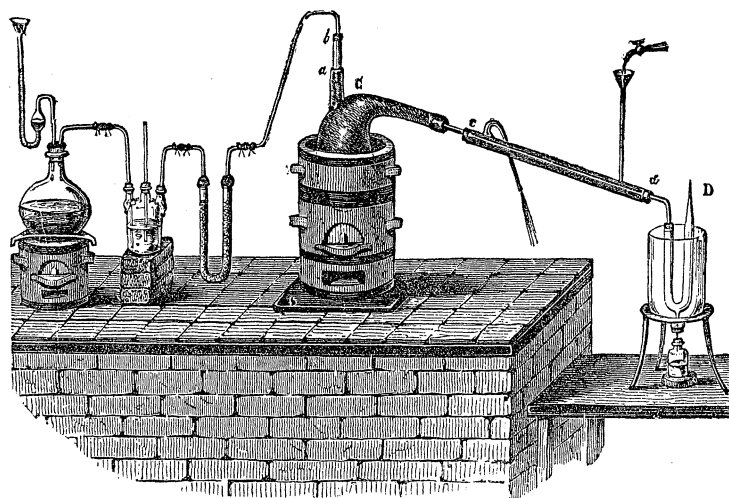


Fig. 538.

ties. The bichloride of titanium thus obtained is yellow, from a certain quantity of chlorine it contains in solution, and is also yet impurified by some sesquichloride of iron. It is obtained pure by shaking it with a small quantity of mercury, which combines with the dissolved chlorine, and then distilling in a glass retort to separate it from the sesquichloride of iron.

Bichloride of titanium is a colourless liquid, giving off thick white fumes in the air. Its density at  $32^{\circ}$  is 1.761, and it boils at  $276.8^{\circ}$ , when the density of its vapour is 6.836. It behaves with water like bichloride of tin, which it closely resembles in its physical and chemical properties. It combines with a small quantity of water and forms a crystallized compound; but a large quantity of water decomposes it by forming a white precipitate of titanous acid, while the liquid contains bichloride of titanium dissolved in a great excess of chlorohydric acid. The precipitate itself dissolves when treated with chlorohydric acid, but again gives off titanous acid by boiling the diluted liquid for some time, when the latter passes into a modification in which it is extremely insoluble in acids.

By passing hydrogen, saturated at the temperature of  $212^{\circ}$  with vapour of bichloride of titanium, through a porcelain tube heated to redness, crystalline spangles of a deep violet colour, consisting of *sesquichloride of titanium*, are condensed in the cold portions of the reducing tube. This compound is deliquescent, and dissolves readily in water, producing a violet-red solution, which is one of the most powerful reducing agents. It precipitates gold, silver, and mercury in a metallic state from their solutions, and reduces

the salts of iron and copper to their minimum of oxidation. It even decomposes sulphurous acid, by setting free the sulphur.

The equivalent of the metal and the composition of titanous acid have been inferred from the analysis of the bichloride of titanium.

#### COMPOUND OF TITANIUM WITH SULPHUR.

§ 954. A compound of titanium with sulphur is known, corresponding to titanous acid, and closely resembling the bisulphide of tin, or mosaic gold. *Bisulphide of titanium*  $TiS_2$  is obtained by passing a current of sulphhydric acid gas, saturated at  $212^\circ$  with vapour of bichloride of titanium, through a tube heated to redness; when the inside of the tube becomes covered with a thick coating of bisulphide of titanium, in the form of scales having a metallic lustre and the colour of brass.

#### DISTINCTIVE CHARACTERS OF THE COMPOUNDS OF TITANIUM.

§ 955. The combinations of titanium are recognised by the above indicated properties of titanous acid, and by the following distinctive reaction:—Titanous acid affords with borax, in the oxidizing flame of the blowpipe, a colourless glass, which assumes a deep blue colour in the reducing flame. Titanium is also recognised by the properties of its bichloride, and by the red metallic dust which the latter leaves when decomposed by ammonia under the influence of heat.

The combinations of titanium may be easily confounded with those of tin, on account of the close resemblance of the salts of these two metals; while they may readily be distinguished by means of the blowpipe, as stannous acid, when heated with charcoal and some carbonate of soda, yields metallic tin, which can be immediately recognised.

#### DETERMINATION OF TITANIUM; AND ITS SEPARATION FROM THE METALS PREVIOUSLY STUDIED.

§ 956. Titanium is always determined in the state of calcined titanous acid. Its separation from the metals we have hitherto studied is effected either by the insolubility of calcined titanous acid in acids, or by the volatility of the bichloride. Titanous acid dissolved in an excess of chlorohydric acid is not precipitated by sulphhydric acid, which property allows its separation from the heavy metals, such as cadmium, tin, lead, bismuth, copper, mercury, gold, silver, platinum, etc., which, under the same circumstances, are all precipitated.

## TANTALUM OR COLUMBIUM, NIOBIUM, PELOPIUM, ILMENIUM.

§ 957. These names have been given to four new metals\* found some few years since in minerals, called *tantalites* and *ytthro-tantalites*; but their properties are not yet sufficiently known to demand description in this work.

### LEAD.

EQUIVALENT = 103.7 (1296.25; O = 100).

§ 958. The lead of commerce is often tolerably pure, and then possesses a great degree of flexibility and malleability. Chemically pure lead is obtained by calcining in a brasqued crucible the oxide obtained by calcining the crystallized nitrate of lead. Lead is a bluish-gray metal, possessing a bright metallic lustre when freshly cut. Its density is 11.445.

Lead is so soft as to be easily cut with a knife, and leaves metallic-gray marks on paper. Being very malleable when cold, it can be beaten into very thin sheets, and drawn out into fine wire, which is so extremely flexible that it can be tied in knots like a hempen string; but, on the other hand, possesses so little tenacity that a leaden wire of 2 millimetres in diameter breaks under a weight of 9 kilogs.

Lead fuses at a temperature of about  $335^{\circ}$ , giving off appreciable vapours at a red-heat, without being, however, sufficiently volatile to be distilled. It may be crystallized by fusion, by the same process as that indicated for sulphur and bismuth, and the crystals, although rarely well defined, may be seen to be regular octahedrons.

Lead soon tarnishes in the air at the ordinary temperature, an extremely superficial layer being formed on it, which is supposed to

\* Tantalum was discovered in 1801, by Hatchett, in an American mineral, for which reason he called it *columbium*; while in the following year it was again discovered in a Swedish mineral by Ekeberg, who gave to it the name of *tantalum*.

Niobium and pelopium were discovered in 1846, by H. Rose.

Ilmenium was recognised as a peculiar metal in 1847, by Hermann. [The existence of ilmenium is yet a matter of dispute, as some chemists, and especially Rose, regard the ilmenic acid found in samarskite as an impure niobic acid.—*W. L. F.*]

be the suboxide  $\text{Pb}_2\text{O}$ ; and when maintained in a state of fusion in the air oxidizes very rapidly. During the first few moments it is covered with an iridescent pellicle, which soon changes into a yellow pulverulent dust, while at a red-heat oxidation advances rapidly. The oxide  $\text{PbO}$  then comes into fusion, and must be run off in order that the oxidation should continue.

Lead oxidizes in damp air and the vapour of acids, even in that of carbonic. Distilled water, likewise, under these circumstances, acts the part of an acid, in consequence of the affinity of water for the oxide of lead; and a sheet of lead dipped into distilled water becomes covered with a pellicle of white hydrated oxide, or hydrocarbonate, which sometimes forms small crystalline spangles, visible with a lens. The water itself contains a quantity of hydrated oxide of lead, sufficient to be detected by being blackened by sulphuric acid. The presence of a small quantity of some salts, chiefly sulphate of lime, prevents the oxidation of lead, for which reason the effects described are not observed in common spring or well water.

Concentrated boiling chlorohydric acid acts but very feebly on lead, and dilute sulphuric acid attacks it only when the air has access to it; while hot concentrated sulphuric acid converts it into sulphate with disengagement of sulphurous acid. Nitric acid, which is the best solvent of lead, acts on it at the ordinary temperature with the evolution of reddish vapours, and forms soluble nitrate of lead.

#### COMPOUNDS OF LEAD WITH OXYGEN.

§ 959. Three compounds of lead with oxygen are known:

A suboxide  $\text{Pb}_2\text{O}$ .

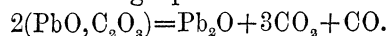
A protoxide  $\text{PbO}$ .

A binoxide  $\text{PbO}_2$ , or plumbic acid.

Again, protoxide of lead and plumbic acid can combine in various proportions, forming several intermediate oxides, called *miniums*, of which red-lead is the most important.

#### *Suboxide of Lead $\text{Pb}_2\text{O}$ .*

§ 960. Suboxide of lead is a black powder obtained by heating the oxalate to a temperature of  $572^\circ$  in an oil-bath, until gaseous carbonic acid and oxide are no longer disengaged. The reaction is represented by the following equation:



The opinion of some chemists, who regarded suboxide of lead as an intimate mixture of metallic lead with protoxide, is shown to be erroneous by the following reactions:—When the suboxide is rubbed with mercury, the latter dissolves absolutely nothing; but solution would take place if any metallic lead existed in the mixture. Again, by treating the suboxide with an aqueous solu-

tion of sugar, no protoxide of lead is dissolved, showing that none exists in the suboxide, as else it would immediately dissolve.

But by treating suboxide of lead with strong acids, even when they are dilute, it is converted into protoxide  $\text{PbO}$  which dissolves, and into metallic lead. A temperature above  $750^\circ$  immediately effects the same decomposition; when the calcined substance parts with its lead to mercury, and with its protoxide of lead to a solution of sugar in water.

Suboxide of lead heated in the air burns like tinder, and is converted into protoxide of lead  $\text{PbO}$ .

*Protoxide of Lead  $\text{PbO}$ .*

§ 961. Protoxide of lead is obtained by the calcination of nitrate or carbonate of lead in the form of a yellow powder, which fuses at a red-heat, and yields, on cooling, a mass composed of crystalline lamellæ, in which state it is called *litharge*, while the name of *massicot* is given to the pulverulent oxide. Well-defined rhombohedral crystals of protoxide of lead are sometimes found in the fissures of lead furnaces. Litharge, when fused in an earthen crucible, readily acts on the latter by combining with silicic acid and perforating the crucible.

Hydrated oxide of lead is obtained by adding ammonia to a cold solution of a salt of lead, when a white precipitate forms, which readily dissolves in a solution of potassa, soda, or ammonia. On evaporating the liquid, the oxide of lead is deposited in the anhydrous state, in the form of brownish-yellow lamellæ, resembling those of litharge. Solutions of baryta and caustic lime may be substituted for those of the alkalies. By adding a concentrated solution of a salt of lead to milk of lime, previously heated to ebullition, the oxide of lead is precipitated in the form of small and very heavy crystals of a beautiful red colour, which are more easily procured by boiling a concentrated solution of caustic soda with an excess of protoxide of lead and allowing the liquid to cool. The red crystals of protoxide of lead retain their colour when they are slowly cooled after the application of heat, but turn yellow when the cooling is sudden. Thus, protoxide of lead may assume very different colours, all varieties of which are found in the litharge of commerce.

Protoxide of lead acts the part of a true acid with powerful bases, and its solution in alkalies should be considered as saline. The compound of oxide of lead with lime has even been obtained crystallized. A solution of oxide of lead in lime is sometimes used for dyeing hair black; which effect is produced by the oxide of lead reacting on the sulphur contained in the organic matter, when black sulphide of lead is formed. The same solution is also used in the manufacture of artificial tortoise-shell.

Protoxide of lead contains

Lead.....	92.83
Oxygen .....	7.17
	<hr/> 100.00

The well-ascertained isomorphism of several compounds of lead with the analogous compounds of baryta and lime, leaves no doubt as to the formula of the protoxide, and it is written  $\text{PbO}$ , whence the equivalent of lead is deduced as 103.7.

*Binoxide of Lead, or Plumbic Acid*  $\text{PbO}_2$ .

§ 962. Binoxide of lead, often called also *puce-coloured oxide of lead* on account of its colour, is prepared by treating heated red lead with dilute nitric acid, which dissolves the protoxide and leaves the plumbic acid in the form of a brown powder. The nitric acid must be renewed until no more oxide of lead is dissolved; after which the plumbic acid is dried at a temperature below  $212^\circ$ . Plumbic acid is also obtained by treating finely divided protoxide of lead suspended in water by chlorine in excess; or by adding a solution of an alkaline hypochlorite to a boiling solution of acetate of lead. A certain quantity of chloride of lead, which in the latter case is precipitated with the plumbic acid, is removed by boiling the precipitate several times with water, in which the chloride is quite soluble.

Plumbic acid contains

1 equiv. of lead.....	103.7	.....	88.47
1 “ oxygen.....	16.0	.....	11.53
	<hr/> 119.7	.....	<hr/> 100.00

Heat readily decomposes plumbic acid, by driving off half of its oxygen and converting it into protoxide of lead. Plumbic acid does not combine with the acids, but gives off a portion of its oxygen to those which are susceptible of superoxidation; when salts of protoxide of lead are formed. It rapidly absorbs sulphurous acid with an elevation of temperature, and forms protosulphate of lead; which property of plumbic acid is often applied to the separation of sulphurous acid gas when mixed with other gases. It also loses one-half of its oxygen when heated with concentrated sulphuric acid, and is converted into the protosulphate. With chlorohydric acid it evolves chlorine and yields protochloride of lead  $\text{PbCl}$ .

Binoxide of lead readily combines with bases forming several crystallizable salts, for which reason it has been called *plumbic acid*. Plumbate of potassa is obtained by heating a mixture of caustic potassa and binoxide of lead entirely freed from protoxide. The binoxide of lead is placed in a silver crucible, and intimately mixed with a highly concentrated solution of caustic potassa; after which it is slowly and gently heated, while, from time to time, a small

quantity of the substance is dissolved in a little water and decomposed by nitric acid. When a copious deposit of plumbic acid ensues, the combination may be considered as effected. A small quantity of water is then poured into the crucible, and rapidly decanted while it is still hot; when the solution deposits, on cooling, colourless and transparent octahedral crystals of plumbate of potassa, of the formula  $\text{KO}, \text{PbO}_2 + 3\text{HO}$ . The alkaline liquid floating above the crystals contains no plumbic acid, because plumbate of potassa is nearly insoluble in cold alkaline solutions. It is decomposed by solution in fresh water.

Plumbates of baryta and lime are obtained as insoluble compounds by heating in the air a mixture of these bases and minium.

*Intermediate Oxides of Lead, Miniums.*

§ 963. By heating finely powdered protoxide of lead, or massicot, in the air at a properly regulated temperature, it absorbs oxygen and is converted in a beautiful orange-red powder, called *minium*.\* The composition of this substance varies according to the prolongation of the roasting; and by continuing it until the minium no longer increases in weight, the product is found to present a composition corresponding to the formula  $2\text{PbO}, \text{PbO}_2$ . It has been accidentally found crystallized in the fissures of a furnace used for the preparation of minium, and presenting the characters of a well-defined compound, the composition of which corresponded to the formula  $3\text{PbO}, \text{PbO}_2$ . Protoxide of lead and plumbic acid may very probably form several definite compounds; but minium should not be considered as a peculiar oxide of lead, as it behaves in all its chemical reactions like a compound of the two oxides just mentioned. When treated with nitric or acetic acid, the protoxide of lead is dissolved, while the plumbic acid is set free; which reaction is generally employed for the preparation of the latter substance.

Minium may be obtained in the humid way, by adding a solution of plumbate of potassa to an alkaline solution of litharge; when a yellow precipitate of hydrated minium is formed, which is converted by desiccation into a red powder of anhydrous minium.

A large quantity of minium is used in the manufacture of crystal glass (§ 686).

In order to prepare minium, powdered litharge is oxidized in a reverberatory furnace at a temperature which should not exceed  $570^\circ$ , the massicot being generally prepared from very pure lead expressly for the purpose. The furnaces have two stories, in the lower one of which, where the temperature is highest, the lead is converted into massicot, always taking care that the temperature

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\* We distinguish commercially two kinds of minium: *orange mineral*, the colour of which is indicated by the name; and *red-lead*, which presents a fine vermilion hue.—*W. L. F.*

does not rise sufficiently high to fuse the oxide of lead, because the converting of litharge which is not in the state of powder into minium by roasting is effected only with great difficulty. The massicot arising from this operation is generally subjected to levigation, to free it from the particles of metallic lead it may contain; after which it is placed in the upper furnace, which is heated only by the waste heat of the lower. It is sometimes simply spread in a thin layer over the floor of the second furnace, its surface being renewed from time to time by stirring it with an iron rod; while, at other times, it is placed in sheet-iron boxes arranged in the furnace. In some manufactories, only one furnace is used for the roasting of the lead and the conversion of the massicot into minium. The lead is first oxidized to litharge, which, after being powdered and levigated, is disposed in flat sheet-iron dishes, which are piled up in the hot furnace. The doors are then closed, and, during the slow cooling of the furnace, the greater part of the massicot is converted into minium. Red-lead of a good quality is then obtained by repeating the operation.

A certain quantity of minium is also prepared by decomposing carbonate of lead, commonly called *ceruse* or *white-lead*, in the air; when a product of a paler colour than that of red-lead, namely, *orange mineral*, is obtained.

#### SALTS FORMED BY THE PROTOXIDE OF LEAD.

§ 964. The protoxide is the only oxide of lead which acts the part of a base with acids. It is a powerful base, the affinities of which are scarcely inferior to those of baryta and lime. It is distinguished among the metallic bases by its tendency to form basic salts, which often present all the characters of definite compounds, the solutions of which turn the red tincture of litmus blue. The salts of lead are poisonous: in small doses they occasion colic and pains in the intestines. Workers in lead, particularly house painters, are highly exposed to the disease called *lead* or *painter's colic*; the best treatment of which consists in administering drinks containing a small quantity of sulphuric acid, or sulphate of soda, in order to convert the oxide of lead into an insoluble sulphate.

#### *Sulphate of Lead.*

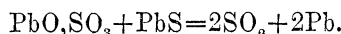
§ 965. Sulphate of lead being insoluble in water, is easily prepared by pouring an alkaline sulphate into the solution of a soluble salt of lead. A large quantity of this product is obtained in the drying-sheds where alum is decomposed by acetate of lead in order to obtain acetate of alumina in solution. Although the sulphate is nearly insoluble in fresh water, it readily dissolves in acid liquids, and particularly in an excess of sulphuric acid. Attention must be paid to this solubility in chemical analyses; in which case the lead remaining in the liquid is separated by a current of sulphuric



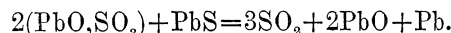
acid, which precipitates it as sulphide. Concentrated chlorohydric acid decomposes sulphate of lead, especially at the boiling point, and transforms it into crystalline spangles of chloride of lead; which reaction proves that in a liquid containing an excess of hydrochloric acid, the chloride of lead is more insoluble than the sulphate.

Sulphate of lead cannot be decomposed by heat; being the only sulphate, among those of the metals of the fourth class which we have now studied which possesses this stability. When heated to a high temperature in an earthen crucible, the sulphate is nevertheless decomposed near the sides of the vessel, by forming silicate of lead by contact with the silex of the crucible. Sulphate of lead is easily reduced by charcoal, the products of decomposition varying with the temperature and proportion of charcoal used. If the charcoal be present in excess and heat applied suddenly, the sulphate is transformed into a protosulphide  $\text{PbS}$ ; but if, on the contrary, the temperature be slowly raised, a considerable quantity of sulphurous acid is disengaged, and the subsulphide of lead  $\text{Pb}_2\text{S}$  is formed. When only the quantity of charcoal absolutely necessary to convert the sulphuric into sulphurous acid and to reduce the oxide of lead is used, perfectly pure metallic lead remains; while with only one-half of this quantity of charcoal, the protoxide  $\text{PbO}$  is obtained.

By heating 1 equiv. of sulphate and 1 equiv. of protosulphide of lead together in an earthen crucible, sulphurous acid is disengaged, and 2 equiv. of metallic lead remain:



But by heating a mixture of 2 equiv. of sulphate and 1 equiv. of sulphide, the sulphur is again disengaged in the state of sulphurous acid, but oxide of lead remains with the metallic lead:



These two reactions are applied in the metallurgy of lead.

Iron and zinc decompose sulphate of lead by placing the metals in acidulated water containing sulphate of lead in suspension; when the lead separates in the metallic state.

By boiling solutions of the alkaline carbonates, sulphate of lead is decomposed and converted into carbonate. The decomposition is much more easily effected by the dry way.

#### *Nitrate of Lead.*

§ 966. Nitrate of lead is prepared by dissolving litharge, or white-lead, or also metallic lead, in an excess of nitric acid, taking care in the latter case to keep the acid in excess. The hot solution, when saturated, deposits regular octahedrons of nitrate of lead on cooling, which are sometimes transparent and sometimes opaque,

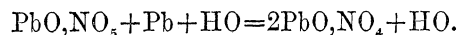
but in each case anhydrous. Cold water dissolves only about  $\frac{1}{4}$  of its weight of nitrate of lead, while it is much more soluble in hot water. Crystals of nitrate of lead decrepitate on hot coals, and feed the combustion, like all the nitrates. Nitrate of lead is decomposed by heat into hyponitric acid which is disengaged, and protoxide of lead which remains. We have seen (§ 118) that this decomposition is applied in the laboratory to the preparation of hyponitric acid.

By boiling a solution of nitrate of lead with the oxide or carbonate of lead, a liquid is obtained which deposits, on cooling, large crystals of a basic nitrate  $2\text{PbO}, \text{NO}_5 + \text{HO}$ .

A nitrate of lead possessing still higher basic properties is obtained by treating the nitrate, or bibasic nitrate, with ammonia, when a white precipitate of the formula  $4\text{PbO}, \text{NO}_5 + 3\text{HO}$  is formed. A large excess of ammonia decomposes the precipitate and leaves hydrated oxide of lead.

#### *Nitrites of Lead.*

§ 967. When thin sheets of metallic lead are digested with the application of heat in a solution of nitrate of lead, a great portion of the lead is reduced without any disengagement of gas, and the liquid assumes a yellow colour, and deposits crystals on cooling, which, when treated with an acid, disengage copious nitrous fumes. Several different salts may be obtained by varying the proportions of metallic lead. By digesting, at a temperature of from  $140^\circ$  to  $176^\circ$ , 1 equiv. of nitrate of lead dissolved in a large quantity of water with 1 equiv. of metallic lead, until the lead is entirely dissolved, a yellow solution is obtained, which, on cooling, deposits large yellow crystalline lamellæ of the formula  $2\text{PbO}, \text{NO}_4 + \text{HO}$ . The reaction producing them is expressed by the following equation :



The crystals are readily decomposed, even when cold, by a solution of carbonate of potassa; when carbonate of lead is precipitated, and the liquid, when allowed to evaporate, deposits successively crystals of nitrate and nitrite of potassa. It is probable from this that the yellow crystals contain no ready formed hyponitric acid, for this does not appear to be able to produce true saline compounds, but that they contain at the same time nitrite and nitrate of lead. Their formula may, therefore, be written  $2\text{PbO}, \text{NO}_5 + 2\text{PbO}, \text{NO}_3 + 2\text{HO}$ .

By digesting 3 equiv. of metallic lead with a solution of 2 equiv. of nitrate of lead, until the former is completely dissolved, a liquid is obtained which deposits small orange-coloured crystals, much less soluble than the yellow lamellæ. The formula of these crystals is  $7\text{PbO}, 2\text{NO}_4 + 3\text{HO}$ : they are also decomposed by the alkaline car-

VOL. II.—Q

bonates, and the solution which results from the reaction yields, on evaporation, alkaline nitrate and nitrite. By considering this compound as containing nitrate and nitrite of lead, we may write its formula  $4\text{PbO},\text{NO}_3+3\text{PbO},\text{NO}_2+3\text{HO}$ . The same compound is obtained by boiling a solution of the yellow salt with oxide of lead.

Lastly, by boiling for a long time with an excess of metallic lead, either a solution of nitrate of lead, or of the yellow or orange-coloured salts just described, small rose-coloured crystals of the formula  $4\text{PbO},\text{NO}_2+\text{HO}$  are obtained, which are, consequently, a quadribasic nitrite of lead. The neutral nitrite of lead is easily prepared with the basic salt, by suspending the latter in water and passing through it a current of carbonic acid gas; when 5 equiv. of oxide of lead are precipitated as carbonate, while the liquid, on being evaporated in vacuo, deposits yellow prismatic crystals of anhydrous neutral nitrite  $\text{PbO},\text{NO}_2$ . By means of this neutral nitrite of lead, the soluble neutral nitrites are easily prepared by double decomposition, by adding to its solution that of the carbonate or sulphate of the base which it is desired to obtain in combination with the nitrous acid.

#### *Phosphates of Lead.*

§ 968. Several compounds of oxide of lead with phosphoric acid are known, corresponding to the modifications of phosphoric acid described § 842. By pouring a solution of ordinary phosphate of soda  $(2\text{NaO}+\text{HO})\text{PO}_3+24\text{HO}$ , into a solution of nitrate of lead, a white insoluble precipitate is obtained, which, however, dissolves readily in an excess of acid or alkali. The formula of the precipitate is  $(2\text{PbO}+\text{HO})\text{PO}_3$ : it melts readily before the blowpipe into a yellow globule, assuming crystalline facets on solidifying; which character is sometimes used as a blowpipe reaction for phosphates.

A basic phosphate  $3\text{PbO},\text{PO}_3$  is obtained by treating the preceding salt with ammonia. The other phosphates have been but little studied.

A phosphate of lead combined with a certain quantity of chloride of lead, which occurs in nature, and is called *phosphate of lead*, crystallizes in regular 6-sided prisms, belonging to the rhombohedral system. Its colour is a more or less greenish yellow, and its formula is  $3(3\text{PbO},\text{PO}_3)+\text{PbCl}$ .

#### *Silicates of Lead.*

§ 969. Oxide of lead and silicic acid combine in all proportions, and form, after fusion, vitreous substances, which have a yellow tinge when the proportion of oxide of lead is considerable. The silicates of lead enter into the composition of glass, and have been treated of under this head (§ 669).

*Aluminate of Lead.*

§ 970. A compound of oxide of lead with alumina occurs in nature, in which the latter substance plays the part of an acid: the formula of the mineral is  $\text{PbO}, 2\text{Al}_2\text{O}_3 + 6\text{HO}$ .

*Chromates of Lead.*

§ 971. The neutral chromate of lead  $\text{PbO}, \text{CrO}_3$  is obtained in the form of a beautiful yellow powder by adding a solution of neutral acetate of lead to one of neutral chromate of potassa. The salt is used in oil-painting, under the name of *chrome yellow*, and also finds application in dyeing. The shade of chromate of lead varies with the more or less perfect neutrality of the salts used in precipitation, and according to the greater or less dilution and the temperature of the liquids. Neutral chromate of lead is found in nature, forming beautiful red prismatic crystals, which yield a yellow powder.

A bibasic chromate of lead  $2\text{PbO}, \text{CrO}_3$  is obtained by fusing neutral chromate of lead with nitrate of potassa; when beautiful red crystals are deposited at the bottom of the crucible. The supernatant nitrate of potassa is decanted, and the crystals of bibasic chromate of lead are washed as quickly as possible.

*Acetates of Lead.*

§ 972. Neutral acetate of lead, which is extensively used in dyeing, is prepared by treating litharge with acetic acid or vinegar, taking care to have an excess of acid, to prevent the formation of basic acetates. The liquid, evaporated slowly, yields large crystals, of which the formula is  $\text{PbO}, \text{C}_4\text{H}_3\text{O}_3 + 3\text{HO}$ . (The formula of acetic acid, at its maximum of concentration, is  $\text{C}_4\text{H}_3\text{O}_3 + \text{HO}$ .) The solution of acetate of lead is perfectly neutral, and absorbs a small quantity of carbonic acid from the air; when the sides of the vessel become covered with a thin deposit of carbonate of lead, while the solution manifests a slight acid reaction. Crystals of neutral acetate of lead part with their water in a dry vacuum, and when heated. After melting in their water of crystallization, which they lose entirely at a temperature of  $212^\circ$ , they undergo the igneous fusion at about  $374^\circ$ ; and, when heated still further, lose a portion of their acetic acid, which is partially decomposed by disengaging carbonic acid, while a basic acetate  $3\text{PbO}, 2\text{C}_4\text{H}_3\text{O}_3$  remains, which is itself decomposed at a higher temperature. Acetate of lead has a sweet taste, which becomes astringent and metallic; and it dissolves in  $\frac{7}{10}$  of its weight of cold water.

By boiling a solution of neutral acetate of lead with a quantity of litharge equal to one-half of that which the acetate contains, a liquid is obtained which, after evaporation, deposits crystals of a basic acetate of lead of the formula  $3\text{PbO}, 2\text{C}_4\text{H}_3\text{O}_3 + \text{HO}$ . By

boiling the same solution with a quantity of oxide of lead equal to that which the neutral acetate contains, a liquid results which yields crystals of a still more basic salt, and of which the formula is  $3\text{PbO}, \text{C}_4\text{H}_3\text{O}_3 + \text{HO}$ .

Lastly, by boiling the solution of the last basic salt with an excess of oxide of lead, a very slightly soluble compound is obtained, which is almost entirely deposited on cooling. Its formula is  $6\text{PbO}, \text{C}_4\text{H}_3\text{O}_3$ .

In medicine, a solution of basic acetate of lead is employed, under the name of *extractum saturni*, or *liquor plumbi subacetatis*, which is obtained by dissolving 2 parts of neutral acetate of lead and 1 part of litharge in  $3\frac{1}{2}$  parts of water, and may, therefore, be considered as containing a mixture of the two sub-acetates  $3\text{PbO}, 2\text{C}_4\text{H}_3\text{O}_3 + \text{HO}$  and  $3\text{PbO}, \text{C}_4\text{H}_3\text{O}_3 + \text{HO}$ . The solutions of the sub-acetates of lead have a very decided alkaline reaction, and turn blue the red tincture of litmus. Carbonic acid decomposes them, and precipitates carbonate of lead, while the liquid contains neutral acetate mixed with a certain quantity of free acetic acid.

#### *Carbonate of Lead.*

§ 973. Carbonate of lead is found crystallized in nature, forming beautiful and highly refracting transparent crystals, belonging to the fourth system of crystallization, and isomorphous with arragonite. The salt is prepared by double decomposition by pouring an alkaline carbonate into the solution of a soluble salt of lead, when a white precipitate is formed, which is the anhydrous neutral carbonate, nearly insoluble in water.

Carbonate of lead is used in oil-painting, under the name of *white-lead*, or *ceruse*. It is prepared by several processes apparently very different from each other, but all consisting in the decomposition of sub-acetate of lead, produced by various reactions, by carbonic acid.

One of these processes, called the *process of Clichy*, from its having been first employed at Clichy, near Paris, consists in dissolving litharge in acetic acid so as to obtain a solution of a basic acetate containing a large quantity of oxide of lead, and decomposing it by the carbonic acid produced by combustion in the furnace which serves to heat the kettles in which acetic acid is saturated with the oxide of lead. To effect this, the air driven across the grate of the furnace by a blowing-machine, is conveyed by pipes into the solution of sub-acetate of lead to be decomposed. In some localities the carbonic acid arising from the earth is used (§ 253). Nearly the whole of the oxide of lead is precipitated in the state of carbonate, while the liquid contains all the acetic acid, which is used to dissolve an additional quantity of oxide of lead, and the fresh solution is again subjected to the action of carbonic acid. The same acid may thus serve for the transformation of an

indefinite quantity of oxide of lead into white-lead; but, a certain quantity of it being invariably wasted in the various manipulations, a small quantity must be added each time.

In England, litharge moistened with acetic acid, or with a solution of neutral acetate of lead, is exposed to a current of carbonic acid gas, produced by the combustion of charcoal; by which means the litharge is in a short time converted into the carbonate of lead.

The greater part of the white-lead used in France is prepared in the Department of the North, by a process first adopted in Holland, and called, for this reason, the *Dutch process*. Sheets of lead, of from 0.12 m. to 0.15 m. wide, and from 0.6 m. to 1.0 m. long, coiled up into a cylinder Z (fig. 539), are placed each in a glazed earthen pot, having two little projections *b, b*, on which the roll of lead rests. Each pot contains at the bottom a small quantity of common vinegar, made from fermented beer, and is covered with a leaden plate *mn* which closes it imperfectly. A large number of pots being arranged in several rows on a layer of stable manure, are covered with straw, and a second

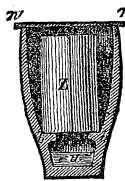


Fig. 539.

row is placed on them, with another layer of manure; which process is continued until 5 or 6 rows of pots are thus arranged. Lastly, the whole is covered with manure, held together by means of boards, so as to allow the air to permeate slowly the whole mass.

The vinegar in the pots yields vapour of water and acetic acid, which, by their contact, rapidly oxidize the metal and cover its surface with sub-acetate of lead. On the other hand, by the fermenting action of the manure, carbonic acid is disengaged and the temperature elevated internally, so that the acid vapours are more and more copiously evolved. The carbonic acid then decomposes the sub-acetate of lead and transforms it into carbonate, while the acetic acid set free effects the formation of a fresh quantity of sub-acetate, which, in its turn, is converted into a carbonate, and so on. In 15 days the operation is terminated, and the disks of lead covering the pots are nearly entirely converted into carbonate. The leaden rolls, which are more or less deeply corroded, are unrolled, beaten to detach the carbonate, and then placed in other pots until they have completely disappeared. The white-lead is finely powdered, purified by levigation, and placed to dry in porous earthen pots.

A certain quantity of sulphate of baryta, or chalk, is often mixed with white-lead, to discover the presence of which the mixture is treated with nitric acid, which dissolves the carbonate of lead and lime and leaves the sulphate of baryta. On evaporating the solution of the nitrates and treating with alcohol, the nitrate of lime is dissolved, while the nitrate of lead remains as a residue.

## DISTINCTIVE CHARACTERS OF THE SALTS OF LEAD.

§ 974. The neutral salts formed by the protoxide of lead are colourless when the acid is free from colour, while the basic salts, on the contrary, are frequently yellow. The soluble salts have a sweet taste.

Caustic potassa and soda yield, when cold, white precipitates of hydrated protoxide of lead, which dissolves in an excess of the reagent.

The alkaline carbonates throw down a white precipitate of carbonate of lead, insoluble in an excess of the reagent.

Sulphydric acid and the alkaline sulphhydrates produce a black precipitate of sulphide of lead, even when the liquid does not contain a great excess of acid, which does not dissolve in an excess of alkaline sulphhydrates.

Solutions of lead yield with the soluble sulphates a white precipitate, insoluble in water, which at first might be confounded with sulphate of baryta, but which is easily distinguished from the latter by being blackened by sulphydric acid.

Prussiate of potash throws down a white precipitate with salts of lead.

By adding chlorohydric acid, or a soluble chloride, to a slightly concentrated and hot solution of a salt of lead, a white precipitate of chloride of lead is obtained, which changes, on cooling, into small crystalline lamellæ of a peculiar aspect. If an iodide be substituted for the chloride, gold-coloured yellow spangles, which are equally characteristic, are obtained.

Iron, zinc, and tin precipitate lead from its solutions in the metallic state.

Lastly, the salts of lead are easily recognised in the blowpipe, because, when heated with carbonate of soda on charcoal, in the reducing flame, they yield a globule of metallic lead, easily recognised as such by its physical and chemical properties.

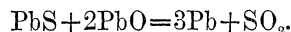
## COMPOUNDS OF LEAD WITH SULPHUR.

§ 975. The sulphide of lead  $PbS$  corresponding to the protoxide  $PbO$ , found in nature in the form of beautiful bluish-gray and brilliant crystals, which mineralogists call *galena*. It is the most common ore of lead, and also the most important, as it furnishes nearly all the lead of commerce. The sulphide is obtained directly by fusing grain lead with sulphur, when the combination takes place with incandescence; but to obtain a pure sulphide, the substance must be pulverized and heated a second time with sulphur. The black precipitate effected by a current of sulphydric acid in a solution of a salt of lead is very finely divided protosulphide.

Sulphide of lead fuses at a red-heat, and, if allowed to cool very slowly, the mass presents after its solidification a crystalline texture, in which the cubic cleavage is easily distinguished. Sulphide of

lead is slightly volatile, and may be sublimed in a porcelain tube in a current of gas; when the colder parts of the tube become coated with small, but extremely brilliant cubic crystals of sulphide.

Sulphide of lead reacts readily in the air, the products varying with the temperature and manner of conducting the operation; and while a great deal of sulphate and oxide of lead is generally formed, a large quantity of metallic lead may also be obtained. We have seen (§ 965) that by heating 1 equiv. of sulphate with 1 equiv. of sulphide of lead, 2 equiv. of metallic lead are obtained with disengagement of sulphurous acid; and again, by heating 1 equiv. of sulphide with 2 equiv. of protoxide, sulphurous acid is disengaged, and 3 equiv. of metallic lead remain:



As will easily be conceived, these various reactions may occur during the roasting of sulphide of lead; and we shall, in fact, meet with examples of this in the metallurgy of lead.

Sulphide of lead is not appreciably acted on by chlorohydric or by dilute sulphuric acid; but concentrated boiling sulphuric acid converts it into sulphate with disengagement of sulphurous acid. Nitric acid, even when diluted, acts readily on galena; and, when the acid is mixed with a sufficient quantity of water, the sulphur is set free, while the lead dissolves in the state of nitrate. Fuming nitric acid converts the sulphide into sulphate; and lastly, nitric acid in a state of medium concentration, transforms a great portion of the sulphide into sulphate, while the remaining sulphide yields free sulphur and lead which dissolves in the state of nitrate.

By heating 1 equiv. of sulphide of lead with 1 equiv. of metallic lead, a *subsulphide of lead*  $\text{Pb}_3\text{S}$  is obtained, which is constantly met with in the metallurgy of lead, where it forms what are called *leaden matts*. Sulphide of lead appears to possess the property of combining with larger quantities of lead.

#### COMPOUND OF LEAD WITH SELENIUM.

Selenide of lead has been found in some mines of galena, chiefly in the Hartz mountains, forming crystalline masses, with cubic cleavage, closely resembling galena. Selenium is extracted from this mineral, by heating in a crucible an intimate mixture of powdered selenide of lead, nitrate, and carbonate of soda, and treating the fused mass with boiling water; when a solution is obtained containing seleniate of soda, which is separated by crystallization. The seleniate is then boiled with an excess of chlorohydric acid, which converts the selenic into selenious acid; and, lastly, the selenium is precipitated by sulphurous acid.

#### COMPOUNDS OF LEAD WITH ARSENIC.

§ 976. Lead and arsenic combine readily, and produce very brittle crystalline compounds.



## COMPOUND OF LEAD WITH CHLORINE.

§ 977. Lead is easily acted on by chlorine, yielding but one compound, the protochloride of lead  $\text{PbCl}$ . Chloride of lead is readily prepared by heating litharge with chlorohydric acid, by which the oxide is transformed into a white crystalline powder, formed of small acicular crystals, or small spangles. The chloride is but slightly soluble, especially in cold water; and is deposited from a hot saturated solution, on cooling, in the form of small crystals, only a small proportion remaining in the mother liquid. Chloride of lead fuses without decomposition before attaining a red-heat, and congeals into a substance resembling horn, and divisible by a knife; while, at a higher temperature, it gives off copious fumes. It may be prepared by double decomposition, by pouring a solution of sea-salt into a concentrated solution of a salt of lead.

Chloride and oxide of lead combine in several proportions, producing oxychlorides, which crystallize readily by fusion, and, on account of their beautiful yellow colour, are used in painting, under the names of *mineral yellow*, *Cassel yellow*, *Turner's yellow*. Cassel yellow, which is prepared by fusing together 10 parts of red-lead and 1 part of sal-ammoniac, consists of large crystalline lamellæ, of the formula  $\text{PbCl} + 7\text{PbO}$ . Turner's yellow is obtained by allowing a paste made with 7 parts of litharge, 1 part of sea-salt, and a certain quantity of water, to rest for several days, and subsequently removing the soda by treatment with water, and fusing the residue in a crucible.

## COMPOUND OF LEAD WITH IODINE.

§ 978. On adding a solution of iodide of potassium to a hot and sufficiently dilute solution of a salt of lead, the liquid deposits, on cooling, yellow crystalline spangles of iodide of lead  $\text{PbI}$ , having the lustre of gold.

## DETERMINATION OF LEAD, AND ITS SEPARATION FROM THE METALS PREVIOUSLY STUDIED.

§ 979. Lead is determined in the state of anhydrous protoxide, or as sulphate. It is frequently precipitated from its solutions in the state of carbonate, and converted into protoxide by calcining to redness; but it is important not to calcine the substance with the filter, as a portion of the lead would then be reduced to the metallic state, and attack the platinum crucible, if the experiment were made in a vessel of this metal. Care must therefore be taken to separate the substance from the filter, and drop it into the crucible, after which the filter is burned at the end of a platinum wire held over the crucible, so that the calcined matter may fall into it. The crucible is then heated to redness over an alcohol lamp; while, for the sake of greater certainty, the substance is moistened with a few

drops of nitric acid, and again calcined. Analogous precautions must be observed during the calcination of sulphate of lead, the sulphate being reduced to sulphide by contact with organic matter.

Lead is separated from the alkaline metals by many of the soluble carbonates and sulphates, or by sulphhydric acid, all of which reagents precipitate only the lead. It is separated from magnesia, alumina, the oxides of manganese, iron, chrome, cobalt, nickel, zinc, etc., by the alkaline sulphates or sulphhydric acid; and from cadmium by the alkaline sulphates, which precipitate only the lead. It is separated from titanium by a current of sulphhydric acid passed through the strongly acid liquid, by which the lead alone is precipitated. In order to separate lead from tin, both metals are precipitated together by an alkaline carbonate, and afterward by calcining the precipitate and treating it with nitric acid, the tin is converted into stannic acid, and the oxide of lead into nitrate of lead; the latter alone is dissolved by treating again with water.

#### TESTING OF LEAD ORES BY THE DRY WAY.

§ 980. Galena, which is the principal ore of lead, is tested by heating to a strong red-heat in an earthen crucible a mixture of 20 gr. of pulverized galena with 30 gr. of black flux and 5 or 6 gr. of small iron nails, called *Paris tacks*; when the galena is decomposed, its sulphur combining partly with the iron and partly with the alkaline matter of the black flux, and the lead separates and forms a button at the bottom of the crucible. After cooling, the leaden ball is extracted by breaking the crucible, and flattened under a hammer, to see that it contains no iron nails, and then weighed. The small quantity of lead remaining in the slag is of no importance in ordinary testing.

#### ALLOYS.

§ 981. Lead forms several alloys used in the arts, the principal of which are, type-metal, composed of antimony and lead, and the alloys of lead and tin used for soldering and in the manufacture of tin utensils.

The alloy used for type-metal corresponds nearly to the formula  $Pb_2Sb$ , and is composed of

Lead.....	76.2
Antimony.....	23.8
	<hr/> 100.0

A small quantity of bismuth is sometimes added.

This alloy is analyzed by means of nitric acid, which dissolves the lead in the state of nitrate, and converts the antimony into antimonious acid. It is evaporated to dryness to drive off the excess of acid, after which water dissolves the nitrate of lead, and leaves the insoluble antimony. As it is difficult to convert the whole of

the antimony into antimonious acid by means of nitric acid, it is preferable to reduce the residue to the state of metallic antimony, by heating it in a glass tube in a current of hydrogen gas. The lead is then determined either differentially, or as sulphate by precipitating the solution containing it by an alkaline sulphate. If the alloy contained bismuth, the residue obtained by evaporating the nitric solution to dryness must again be treated with water acidulated with nitric acid, in order to dissolve the lead and bismuth; after which the liquid is carefully saturated with ammonia, which would precipitate the bismuth without precipitating the lead, unless a great excess were added. The perfect separation of lead and bismuth is difficult.

Lead and tin combine readily in all proportions; and the fusibility of the alloys formed greatly varies according to the proportions of the two metals.

Pure lead fuses at.....	635.0°
The alloy $\text{Pb}_3\text{Sn}$ “ .....	552.2°
“ $\text{PbSn}$ “ .....	465.8°
“ $\text{PbSn}_2$ “ .....	384.8°
“ $\text{PbSn}_3$ “ .....	366.8°
“ $\text{PbSn}_4$ “ .....	372.2°
“ $\text{PbSn}_5$ “ .....	381.2°
Pure tin “ .....	437.0°

Thus the most fusible alloy corresponds to the formula  $\text{PbSn}_3$ , and fuses at a temperature lower than that of the most fusible metal which enters into its composition. These alloys are easily destroyed by eliquation (§ 315).

For tin-ware, tin is alloyed with 12 or 18 per cent. of lead, by which the metal is rendered harder and more easy to be worked in a lathe.

Plumber's solder is composed of

Tin.....	1 part.
Lead.....	2 “

This solder fuses at about 527°.

Tin-worker's solder contains

Tin.....	1 part.
Lead.....	1 “

The alloys of tin and lead are easily analyzed. It suffices to attack the alloy with nitric acid, which dissolves the lead and converts the tin into insoluble stannic acid; when the tin is determined in the state of calcined stannic acid, and the lead differentially.

#### METALLURGY OF LEAD.

§ 982. A great number of minerals containing lead are found in nature, the principal of which are sulphide of lead or galena, the selenide, carbonate, chlorophosphate, and chromate. The sulphide

and carbonate of lead are the only minerals sufficiently rich to be worked to advantage.

Galena is generally found in veins traversing the primitive and transition rocks, and also often forms pipe-veins of greater or less size in the transition rocks and the lower stage of the secondary rocks. Lastly, certain sandstones, belonging to the variegated sandstone (*bunter sandstein*) formation, are impregnated with small grains of galena, which are easily separated mechanically, when the sandstone is not too hard.

Galena always undergoes a mechanical preparation. The ore is first sorted by hand, and the pieces sufficiently rich are smelted immediately, while the remainder is crushed between cylinders and sifted. A fresh quantity of ore fit for melting is thus obtained, besides an ore closely mixed with gangue, which is stamped, and then washed in boxes or on tables. These preparations yield a sludge of greater or less fineness of grain, which is sent to the smelting-house.

Galena often contains enough silver to allow it to be extracted with advantage; and its metallurgic treatment is then directed to the extraction of both the lead and silver. Some galenas are mixed with copper pyrites, and then yield a sufficient quantity of copper to make them valuable for the extraction of that metal.

Carbonate of lead forms small pipe-veins in the secondary rocks, and exists most frequently in the vicinity of the galena-mines. Its metallurgic treatment is very simple: it is fused, in contact with charcoal, in small blast-furnaces, called *elbow-furnaces*; when the lead is reduced and easily separated from the slag.

The most common gangue of lead-ore is quartz, carbonate of lime, sulphate of baryta, and fluor-spar. Care must be taken that the melting-bed contains substances essential to an easy fusion of the slag; for which reason it is often necessary to add foreign substances, in order to obtain more fusible scoriæ.

§ 983. The metallurgic processes by means of which lead is extracted from galena are divided into two classes:

In the first, the ore is smelted with metallic iron, which separates the sulphur from the lead and forms a fusible sulphide of iron, while the lead is set free. Theoretically, the mixture for smelting should be:

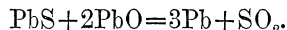
1 equiv. of sulphide of lead.....	109.7
1 “ “ iron.....	28.0
	<hr/> 147.7

From which are obtained

1 equiv. of lead.....	103.7
1 “ sulphide of iron.....	44.0
	<hr/> 147.7

The second method is founded on the reactions already mentioned (§ 965).

By fusing together 1 equiv. of sulphide of lead and 2 equiv. of oxide of lead, 3 equiv. of metallic lead are obtained, while 1 equiv. of sulphurous acid is disengaged:



By melting together 1 equiv. of sulphide and 1 equiv. of sulphate of lead, 2 equiv. of sulphurous acid are disengaged, while 2 equiv. of metallic lead are obtained.

The process founded on the reactions, and called the *process by reaction*, consists in roasting the galena in a reverberatory furnace until a certain quantity of oxide and sulphate is formed, and then giving a blast, after having intimately mixed the material and closed all the doors of the furnace. During this second period of the operation, the reaction between the sulphate and sulphide takes place, and the lead is separated.

§ 984. The reduction of galena by iron is used especially in the case of ores which are accompanied by a very siliceous gangue, and which are not very amenable to the process by reaction, because a great part of the oxide of lead combines with the siliceous gangue and no longer reacts on the sulphide. The process by iron is employed to a great extent on the Hartz Mountains; and the following is the plan adopted in the smelting works of Clausthal:

A melting-bed is made of sorted ores and sludges, which are mixed with granular cast-iron, and with various secondary products of the further treatment of the ores, the origin of which we shall successively explain. The charge is generally composed of

- 34 cwt. of sorted ore and sludge, containing 24 cwt. of pure galena.
- 4 to 5 “ of the debris of the cupelling furnaces, which is strongly impregnated with litharge.
- 1 “ of scrapings (*abstrich*) of cupellation.
- 39 “ of slag arising from a first fusion of the ore, or yielded by the fusion of the leaden stones, or matts, the object of which addition is to assist the fusion of the gangues.
- 1½ “ of granular cast-iron.

The fusion is effected in a blast-furnace (figs. 540, 541, 542, and 543), about 18 or 20 feet high, and measuring 3 feet at its greatest width. At the bottom of the hearth is a crucible which partly projects from the furnace, the base of which is formed of two blocks of sandstone, making a gutter, on which a mixture of clay and charcoal\* is heaped, so as to form a cavity which extends beyond the

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\* Two different mixtures of clay and charcoal are employed in various operations occurring in the German methods of smelting: one consisting of 2 parts of

furnace. A tap-hole opening at the lower part of the crucible permits the escape of the liquid products which have there accumulated; and they are led into a second crucible E, which is wholly external. The furnace receives the blast of two tuyers arranged on the opposite side of the tump.

Fig. 540.

Fig. 541.

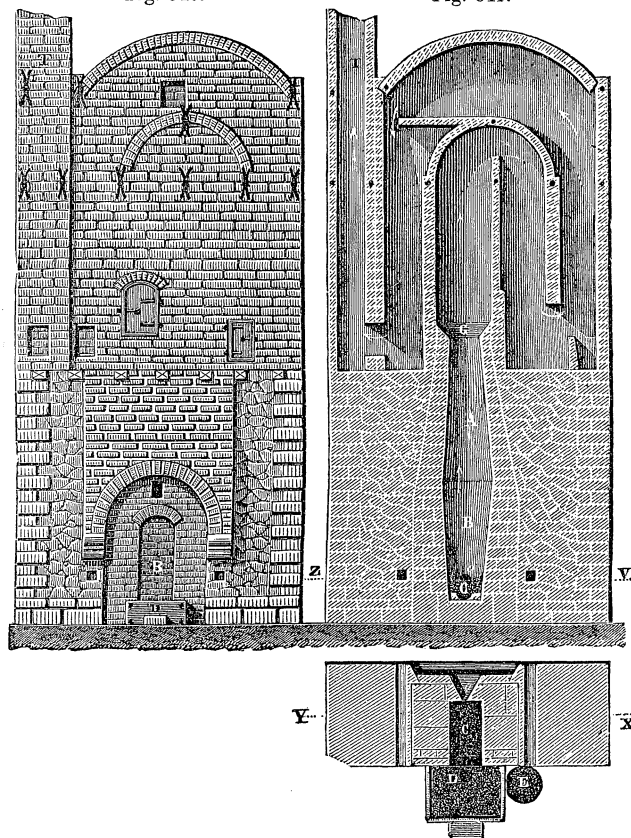


Fig. 542.

The ore is charged on the side of the tuyers, and the fuel on that of the centre-vent. As slag suddenly cooled by the cold air always adheres around the tuyers, the workman arranges them so as to form a canal which projects for about 6 inches into the furnace, and thus makes a prolongation of the tuyer, which he calls the *nose*

clay and 1 of charcoal, called *schweres gestuebbe*; and one containing 1 of clay and 2 of charcoal, called *leichtes gestuebbe*. The first I shall, in the following, translate by *heavy brasque*, and the second by *light brasque*.

To the "leaden stones" (*bleistein*) I shall give the French name of *matt*.—W. L. F.

of the tuyer. The object of the nose is to convey the air immediately upon the fuel, and prevent it from first passing through the ore, which would be thus exposed to an oxidizing action, and part with a great deal of oxide of lead to the scorixæ. The smelter must also be careful to give a proper shape to the nose of the tuyer, and to modify it according to the blast of the furnace.

The temperature must not be very high in the upper part of the furnace, as otherwise a large proportion of galena would be volatilized. In all cases, the gases pass, on leaving the throat G, and before reaching the chimney T, several condensing-chambers arranged above the smelting-furnace; where a plumbiferous dust is copiously deposited, which is carefully collected and thrown into the melting-beds.

During the smelting, the scorixæ flow off continually, an assistant detaching those which have become solid, and drawing them out with a hook. When the inner basin is full of metallic products, the canal communicating with the basins D and E is opened; when the substance flows into the external crucible E, and there divides into two layers; the inferior layer being metallic lead, and the upper stratum consisting of subsulphide of lead  $Pb_2S$ , mixed with other metallic sulphides which existed in the ore, and with that of iron arising from the reaction of the metallic iron on the galena. This substance, which is called *the first leaden matt*, soon solidifies, and is then withdrawn with a hook and set aside. The workman then removes the lead with a ladle, and runs it into moulds which give it the shape of lenticular disks. The poorest scorixæ, that is, those least rich in lead, are rejected, while those which float on the matt in the pot, and which always contain

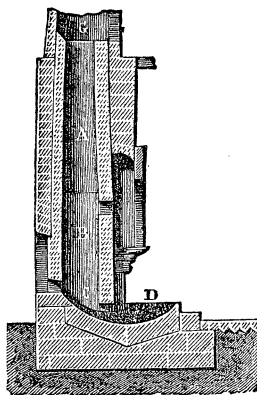


Fig. 543.

some grains of lead, are set aside to be added to a subsequent charge; though poor scorixæ are sometimes used for this purpose when rich scorixæ are wanting. The charges, or smelting-beds, the composition of which we have just indicated, yield 19 cwt. of lead, and 7 or 8 cwt. of the first leaden matt, containing from 2 to  $2\frac{1}{2}$  cwt. of lead.

§ 985. The first matts are collected in the foundry, and when there is sufficient quantity of them to be worked up, they are roasted in heaps on a layer of fuel; when a large portion of the sulphur is disengaged in the state of sulphurous acid. The roasting lasts for 3 or 4 weeks; after which the material is sorted, and, while the pieces sufficiently roasted are considered as ready for smelting, the others are again roasted. Four successive roastings are necessary for the proper preparation of the material.

A charge of matt is composed of

- 32 cwt. of roasted matt.
- 32 “ of rich scorïæ, arising from the smelting of the ores.
- 4 or 5 “ of debris of cupellation.
- 2 “ of scrapings, (*abstrich.*)
- 2 “ of scorïæ arising from the reduction of litharge.
- 1 “ of granular cast-iron.

The roasted matts are smelted in an elbow-furnace, which is a small blast-furnace (figs. 544, 545, and 546), about 4.5 feet in height, widened at its upper part C. Fig. 546 represents a horizontal section of it made at the height of the tuyer, while fig. 545 shows a vertical section through the line XY of the plane (fig. 546); and lastly, fig. 544 gives an anterior view. The furnace is fed by a

Fig. 544.

Fig. 545.

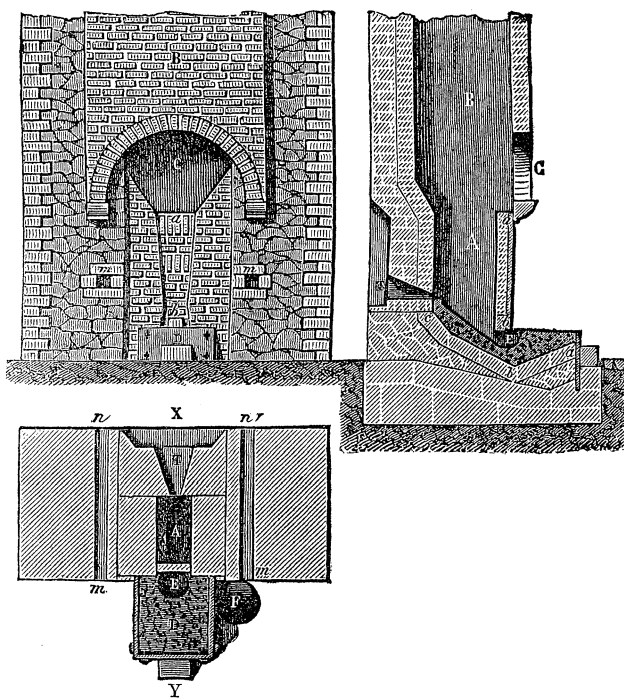


Fig. 546.

single tuyer T, at the extremity of which a nose of 4 inches in length is allowed to form. At the bottom of the furnace is a brasqued crucible E, projecting partly from the furnace, and communicating, by means of a canal, with an external crucible F, placed on a lower level.—Coke is the fuel used.



By the roasting of the matt, a large portion of the sulphide of iron has passed into the state of oxide, which, during the fusion in the elbow-furnace, combines with the silicates of the scorïæ and with the ashes of the fuel, forming very fusible scorïæ, which flow constantly from the furnace. The sulphide of lead is reduced by the metallic iron, and a fresh quantity of lead and a second matt analogous to the first are formed. When the matt is solidified it is removed and set aside to be again worked, while the metallic lead is run into disks.

A smelting-bed of first matt, composed as we have indicated, yields 12 cwt. of lead and 8 cwt. of second matt.

The second matts are subjected to a similar treatment, being subjected to 3 or 4 successive roastings, and then passed through the elbow-furnace, with additions similar to those of the first. A certain quantity of metallic lead is thus obtained, and a third matt, which is roasted in its turn and melted in the elbow-furnace, yielding an additional quantity of lead and a fourth matt.

The affinity of the copper existing in the original ore for sulphur being greater than that of the lead, the former passes indefinitely into the matts; so that the metal, which is found in a very small quantity in the original ore, is concentrated in the fourth matt in sufficient quantity to make it a very rich ore of copper, and capable of being advantageously worked. It is called the *copper matt*.

§ 986. When the gangue of the galena is but slightly siliceous, the process by reaction is preferred. It is adopted in England, in Carinthia, and the majority of the lead-foundries in France, particularly at Poullauen in Brittany, and Pont-Gibaud in Auvergne.

The ore is deposited in the state of sludge on the floor of a reverberatory furnace (figs. 547 and 548) of about 9 or 12 feet in length,

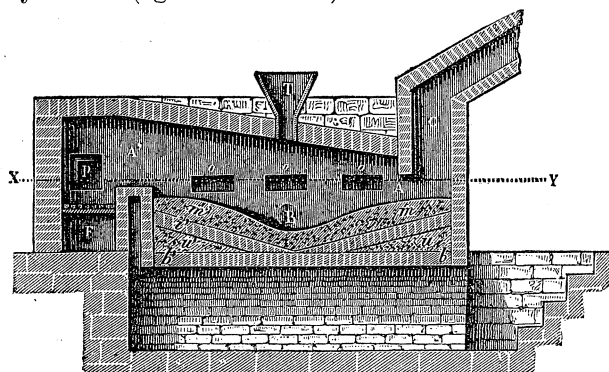


Fig. 547.

and nearly the same width, formed either of pulverized scorïæ or of a slightly siliceous clay. In the centre there is an excavation B,

in which the fused lead collects, and whence it flows through a small canal into cast-iron pots G. The charge is inserted through an

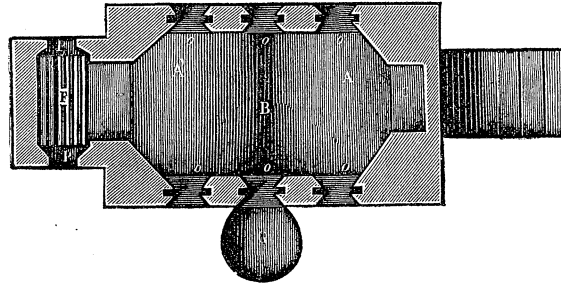


Fig. 548.

upper aperture T, furnished with a hopper. Three lateral openings *o, o, o* are made in both of the opposite faces of the furnace, and serve as working-holes. Pit-coal is burned on the grate F; and the flame and current of hot air, after having passed through the furnace, traverse long condensing chambers, in which they deposit the substances carried over mechanically or by volatilization.

The quantity of ore treated in the furnace at a time varies in different foundries: 20 or 25 cwt. are used in England. The ore is spread evenly over the floor, and roasted from 2 to 4 hours at a dull red-heat; when sulphurous acid is disengaged, while a large quantity of oxide and sulphate of lead is formed. The workman stirs it frequently, in order to hasten the roasting, at the end of which operation the working-doors are closed and a blast of air is admitted. The unaltered sulphide of lead then reacts on the oxide and on the sulphate; metallic lead and also the subsulphide  $Pb_2S$ , which forms a very fusible plumbeous matt, are separated. The fused substances collecting in the inner excavation are allowed to run out after some time, after which the material remaining on the floor is again roasted by opening the working-doors, and stirring the mass with iron rods, while the temperature of the furnace is at the same time allowed to fall. The doors are then again closed, and, another blast of air being admitted, an additional quantity of metallic lead is reduced. These alternate operations are several times repeated.

In some works small quantities of lime are from time to time thrown on the floor, in order to lessen the fusibility of the slag; while in others powdered charcoal is added at a certain period, in order to decompose the oxysulphides of lead which form, and retard the roasting when it progresses too rapidly. Toward the close of the operation, when the greater part of the lead has run off, there remains on the hearth a scorified slag, impregnated with metallic

lead; a large portion of which is separated by admitting a blast, and allowing the furnace to cool slowly. This last stage of the operation is called the *sweating*. The whole operation requires 7 or 8 hours in England, and 12 or 16 in France.

The matts arising from the reverberatory furnace are added, in the English works, to the roasting of a fresh quantity of ore; while in most of the continental works they are passed through an elbow-furnace.

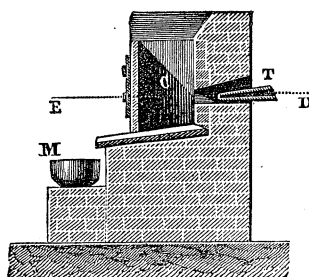


Fig. 549.

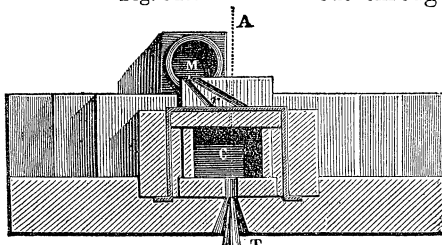


Fig. 550.

The matts are frequently roasted in a heap, and then smelted, after a proper addition of scoriæ, in a very low elbow-furnace, called a *Scotch hearth*, in which a reaction takes place between the sulphate, the oxide, and sulphide of lead, while metallic lead, a matt, and scoriæ are obtained. Fig. 550 represents a horizontal section of a Scotch furnace; and fig. 549 shows a vertical cut through the line AB in fig. 550.

The furnace is only 3 feet in height; and the blast is furnished by a single tuyer T. The metallic lead and matt are collected in a cast-iron pot M. The workman removes, from time to time, the slag which accumulates at the bottom of the furnace, and as it contains

a considerable quantity of lead, he throws it back into the furnace.

§ 987. The lead arising from these different processes often contains enough silver to allow the extraction of the latter to be made to advantage, and is then called *pig-lead*, (*werklei*.) The silver is separated by the process of *cupellation*, which is founded on the property of lead to oxidize when heated in contact with the air, while the silver, which remains unaltered, concentrates indefinitely in the lead which remains in the metallic state, and is left isolated at the end of the operation, when all the lead is oxidized. In order to accelerate the oxidation of the lead, the litharge formed must be removed as fast as it is produced, for which purpose the temperature is kept sufficiently elevated to fuse the oxide of lead. As the melted metal forms a convex surface, the litharge flows constantly into the space between the metal and the side of the vessel, and the litharge runs off as it is formed, without the loss of any metallic lead, through little gutters cut into the side of the vessel, which are made deeper as the level of the metal sinks.

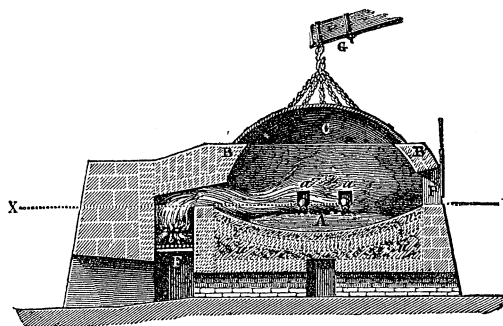


Fig. 551.

Figs. 551, 552, and 553 represent a cupelling-furnace, used at Clausthal in the Hartz. Fig. 552 gives a horizontal section, made at the height of the line XY of fig. 551; and fig. 551 represents a vertical section made through the plane passing through the line ED of fig. 552. Lastly,

fig. 553 furnishes an interior view of the furnace. The cupelling-furnace is a kind of reverberatory, consisting of a lateral hearth F, and a circular one A, the floor of which, having the shape of a spherical cap, is composed of bricks *ii*, placed edgewise on a base *uu* of scorix. It is lined internally with a layer of marl *mm*, which is carefully heaped, and renewed at each operation, and which constitutes the *cupel* properly so called. The arch of the oven is formed of a riveted sheet-iron cover C, lined with clay, and suspended, by means of chains, to a crane GG'G'', by which it can be easily raised and replaced.

The furnace has four openings: that by which the flame from the hearth is introduced; two openings *a*, *a'*, which receive the nozzles

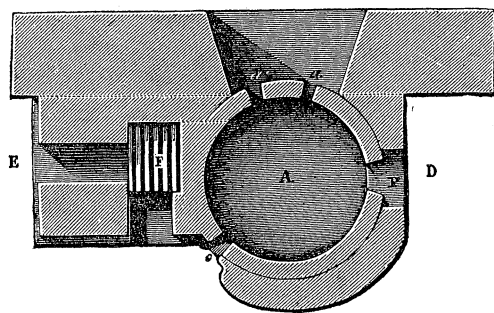


Fig. 552.

of two bellows which constantly drive air over the surface of the bath, and assist the oxidation, while, at the same time, they remove the litharge from the surface; the aperture P, serving for the introduction of the disks of lead; and lastly, the opening *o*, which is the tap-hole for the

litharge. At the commencement of the operation, this last opening is closed by the cupel, but the latter is gradually notched, so as to keep the spout on a level with the bath of metal. The litharge flowing from the hole *o* accumulates at L on the floor of the foundry, where it solidifies.

The cupel must be arranged before commencing the process, for which purpose the cover is removed, and the old cupel, being strongly impregnated with litharge, broken into pieces, which are added to the charges of the ores and matts, as stated in §§ 984

and 985. The brick floor *ii* is moistened with water, and successive layers of marl are beaten down upon it with a stamper.\* The cover then being replaced, all the joints are accurately luted with clay.

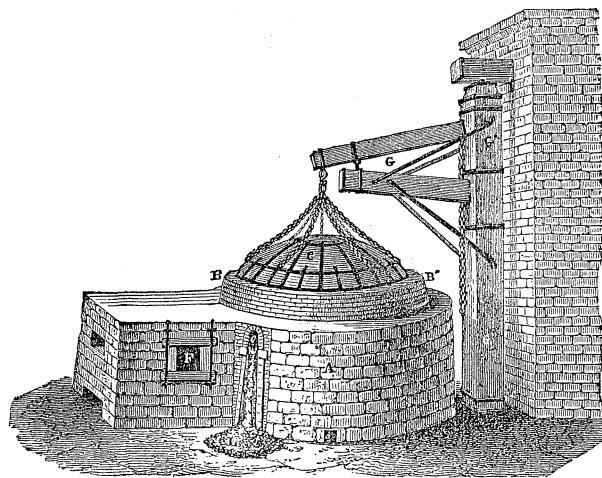


Fig. 553.

One hundred and sixty cwt. of lead being introduced into the furnace, and heat applied, the metal soon comes into fusion; and the bellows then being gently worked, the oxidation commences, and the surface of the bath becomes covered with a black dust of oxide of lead, mixed with foreign substances. The dust, which is infusible at the temperature applied, constitutes the scrapings, (*abstrichs*.) The workman throws from time to time a small quantity of powdered charcoal on the bath, and, by means of a billet of wood placed crosswise at the end of an iron rod, removes the abstrichs from the furnace. After some time, the fused litharge begins to appear; and after the first portions, which, being impure, are allowed to flow off, and are set aside, comes the pure litharge, called *merchantable litharge*, which can be sold in this state, when it is not mixed with the former. The cupellation is continued, the blast being gradually increased to accelerate the oxidation, until all the lead is converted into litharge, and the silver remains isolated in the shape of a disk.

At the moment when the oxidation is arrested, and consequently when the cupellation is finished, a peculiar phenomenon is mani-

\* A layer of marl about an inch in thickness being stamped down, its surface is again loosened by means of an iron rake, to the depth of about half an inch, before the next layer is heaped on; as without this precaution the layers would form successive strata by the heat of the furnace, and not a consolidated mass.—*W. L. F.*

fested, called the *brightning*. During the whole period of oxidation, the metallic bath appears to be more brilliant than the sides of the furnace; and its temperature is in fact higher, since it shares not only that of the surrounding space, but also takes advantage of all the heat developed by the chemical combination of the lead with oxygen. But when the lead is completely oxidized, the second source of heat disappears, the small disk of metallic silver falls rapidly to the temperature of the oven, and its original brilliancy is replaced by a dull colour. On the other hand, at the moment when the last traces of lead are oxidized, there exists only on the brilliant surface of the metallic bath a pellicle of melted litharge, which rapidly grows thinner, presenting the rapid succession of colours of a soap-bubble, and at last tears like a veil, displaying the surface of the metal. The name of *brightning*, or *fulguration*, is given to this rapid succession of optical phenomena.

As soon as the brightning appears, the workman pours first hot and then cold water on the hearth, and then removes the cake of solid silver. The silver, called *cupel silver*, which is not pure, but contains about  $\frac{1}{16}$  of lead, is afterwards *refined*, as will be described when treating of silver.

A cupellation generally lasts 30 hours, including the time necessary for the arrangement of the cupel.

The cupellation of 160 cwt. of pig-lead, arising from the smelting of the schlichs, yields at Clausthal,

- 56 marcs of silver, (a marc =  $\frac{1}{2}$  pound.)
- 118 cwt. of litharge.
- 21 “ of debris of cupellation, (German, *heerd*.)
- 15 “ of scrapings.
- 6 “ of rich litharge.

The rich litharge, which is that obtained during the last stage of cupellation, is not mixed with the rest because it contains a considerable quantity of silver.

160 cwt. of pig-lead, arising from the smelting of the matts, yield

- 62 marcs of silver.
- 112 cwt. of litharge.
- 21 “ of debris of cupellation.
- 18 “ of abstrich.
- 9 “ of rich litharge.

Wood is the fuel used in cupellation.

The litharge arising from cupellation is reduced to metallic lead, a small quantity only being sold as litharge. The conversion of litharge into metallic lead, which is called the *revival of the litharge*, is effected by smelting the litharge in contact with charcoal in an elbow-furnace, furnished with an outer crucible. The scorixæ arising from this fusion are added to the charges of ore, and the lead, after being run into bars, is sent to market.

§ 988. Silver can be advantageously extracted from pig-lead by direct cupellation, only when it contains at least  $\frac{1}{5000}$  part of silver; but latterly, much poorer lead has been profitably worked, by first subjecting it to a process called *refining by crystallization*.<sup>\*</sup> This operation, which separates the lead into very poor lead and into such sufficiently rich for cupellation, is based on the following principle:—By allowing a large quantity of melted argentiferous lead to cool slowly, and frequently stirring the liquid mass with an iron spatula, a crystalline powder of a poor lead is soon formed, which may be skimmed off as fast as it is produced; and by thus successively separating a portion of the lead in the state of imperfect crystals, the greater part of the silver is left in the metal remaining fluid, which thus becomes much richer. By properly repeating these operations, either on the mass which has been removed in the solid state, or on the portion poured off in the liquid state, on the one hand a poorer and poorer lead is obtained, and on the other, lead which is more and more rich in silver. Only that lead which contains a proper quantity of silver is subjected to cupellation, the remainder being sold.

§ 989. Metallic lead is technically used in the shape of sheet-lead, for roofing houses, lining bathing-tubs, making gutters and spouts for conveying water, etc. etc. In the manufacture of sheet-lead, the melted metal is allowed to run over a marble table into plates, the size of which is regulated by wooden rulers, and which are then passed through rollers.

The rolling-machine is composed of two cast-iron cylinders, the lower one of which alone is turned by machinery, while the upper one is carried round simply by adhesion, the pressure it exerts on the sheet of lead being regulated by a counter weight. Return screws, which fasten the upper boxes of the two gudgeons, limit the elevations of the cylinder, and regulate the thickness of the sheet; and, as the screws work independently of each other, the side on which the plate is least rolled may be tightened, so as to obtain a uniform thickness. On each side of the cylinders are tables furnished with iron rails, which receive and guide the sheets. Five or six sheets are rolled, and then passed in an opposite direction between the cylinders, their motion being reversed; which is repeated until the sheets have acquired the requisite thickness.

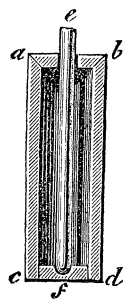


Fig. 554.

Leaden pipe is made on a iron mandrel between grooved cylinders, after having been run into a cast-iron mould, *abcd* (fig. 554), in the axis of which is an iron mandrel *ef*, of the proposed diameter of the leaden pipe. A thick leaden-tube, of from 2.0 to 2.3 feet in length, is thus obtained, and is then fastened on an iron mandrel of

<sup>\*</sup> Commonly known as *Pattinson's process*.—*W. L. F.*

the same diameter as that *ef* of the mould, after which the whole is drawn out between cylinders resembling those used for the drawing of iron-wire. The sides of the pipe are thus reduced in thickness until it attains the length required.\*

#### MANUFACTURE OF LEAD-SHOT.

§ 990. Lead alloyed with 0.3 to 0.8 per cent. of arsenic is generally used in the manufacture of lead-shot; the addition of this small quantity of arsenic giving the lead the property of forming perfectly spherical globules. A sheet-iron sieve is used, shaped like a spherical cap, and pierced with holes of the size of the shot to be made. The dross which forms on the fused lead is first pressed into the sieve, so as to completely line its sides, and the melted metal, being then poured in by small quantities with a spoon, filters through the dross and drops from the perforations. The drops, which should be made to fall from a great height, in order to become solid during their descent, are collected in a reservoir of water; a greater elevation being required according to the size of the shot. The shot, being sorted into sizes by means of sieves, is polished by causing it to revolve in wooden barrels with a small quantity of plumbago.

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\* The new method of making lead-pipe consists of a powerful press, which forces the lead in a heated and soft state out of an opening in an iron reservoir, having a solid and short mandrel of iron in the centre of the opening, of the same diameter as the interior of the tube to be made. The lead is perfectly hard when issuing from the opening, and presents a tubing of a fine glaze interiorly and exteriorly. By this machine also tubes of any length may be manufactured.—*J. C. B.*



## BISMUTH.

EQUIVALENT = 213 (2662.5 ; O = 100).

§ 991. The bismuth\* of commerce is never absolutely pure ; but, as the foreign metals with which it is alloyed are generally more oxidizable than itself, it may be purified by heating the pulverized metal with  $\frac{1}{10}$  of its weight of nitre in an earthen crucible. The temperature should be gradually raised until the nitrate is decomposed ; when the foreign metals oxidize and combine with the potassa as well as a portion of the bismuth, the remainder of the latter being left as a button at the bottom of the crucible.

In order to obtain bismuth chemically pure, a mixture of sub-nitrate of bismuth and black flux must be fused in a crucible.

Bismuth is a grayish-white metal, having at the same time a very decided reddish shade, which is easily seen by placing a piece of bismuth alongside of a specimen of a white metal, such as zinc, antimony, etc. Its density is 9.9. It presents a crystalline fracture with large glittering lamellæ, has but slight malleability, and crystallizes readily by fusion. Beautiful crystals may be obtained by fusing in an earthen capsule some kilogrammes of bismuth of commerce, purified by fusion with nitre, and allowing to cool very slowly. To effect this, the capsule is placed on a bath of heated sand, and covered with a sheet-iron plate, on which burning charcoal is placed. In a short time a hole is made in the solid crust which forms on the surface, and the liquid metal is allowed to run off. The crust being carefully removed, a geode of very beautiful crystals, frequently of several centimetres in diameter, is displayed. These crystals, which are cubes, or rather pyramidal figures resembling those of sea-salt (493), exhibit very elegant iridescent colours, produced by the very thin pellicles of oxide which form on the surface of the metal as it is brought, while hot, in contact with the air. The pellicles present the play of thin scales or soap-bubbles.

Bismuth fuses at  $507.2^{\circ}$  ; and a thermometer plunged into melted bismuth marks this temperature during the whole period of its solidification. Like water, bismuth expands at the moment of solidifying, and is therefore lighter when solid than when liquid. It is volatile at a very high temperature, but nevertheless difficult to distil.

Bismuth remains unchanged in a dry atmosphere, but when exposed to damp air, becomes covered with a very thin pellicle of

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\* Bismuth was known to the ancients, who often confounded it with lead and tin. Stahl and Dufay first proved it to be a peculiar metal.

oxide after some time. Heated in the air, it burns with a small bluish flame, giving off yellow fumes. Bismuth decomposes water only at a very high temperature, and effects no decomposition of cold water in the presence of powerful acids. Concentrated chlorohydric acid acts on it with difficulty, while sulphuric acid attacks it only when concentrated and hot, with disengagement of sulphurous acid. Nitric acid attacks it very energetically, and dissolves it completely.

## COMPOUNDS OF BISMUTH WITH OXYGEN

§ 992. Bismuth forms two compounds with oxygen :

1. An oxide  $\text{BiO}_3$ ;
2. An oxide  $\text{BiO}_5$ , or bismuthic acid.

An intermediate oxide  $\text{BiO}_4$  is known, but should be regarded as a compound of the two preceding, and its formula should be written  $\text{BiO}_3, \text{BiO}_5$ .

*Oxide of Bismuth*  $\text{BiO}_3$ .

§ 993. The oxide of bismuth  $\text{BiO}_3$ , which is obtained by roasting the metal in the air, or better still, by decomposing the basic nitrate of bismuth by heat, presents the appearance of a bright-yellow powder, fusible at a red-heat, and producing on solidification a deeper yellow glass, which readily perforates earthen crucibles. The oxide of bismuth is fixed, and its density is 8.45.

The oxide can be obtained hydrated in the form of a white powder, by decomposing the basic nitrate by an alkali, or by ammonia. On boiling the hydrate in a solution of potassa, it parts with its water, and is converted into a yellow crystalline powder, which is the anhydrous oxide.

The chemical composition of the oxide is,

Bismuth .....	89.87
Oxygen .....	10.13
	<hr/>
	100.00

Some chemists, regarding this oxide as formed of 1 equiv. of the metal and 1 of oxygen, write its formula  $\text{BiO}$ , and adopt for the equivalent of the metal the number 71, which is given by the proportion :

$$10.13 : 89.87 :: 8 : x, \text{ whence } x=71.$$

But as this hypothesis is contrary to all analogy, and is sustained by no example of isomorphism, we shall assign to oxide of bismuth the formula  $\text{BiO}_3$ , and the equivalent of the metal will be deduced from the proportion :

$$10.13 : 89.87 :: 24 : x, \text{ whence } x=213.$$

*Bismuthic Acid*  $\text{BiO}_5$ .

§ 994. Bismuthic acid  $\text{BiO}_5$  is prepared by passing a current of chlorine through a concentrated solution of potassa in which very finely divided oxide of bismuth is suspended; or by heating for a long time in the air a mixture of potassa and oxide of bismuth; or better still, by calcining a mixture of oxide of bismuth, caustic potassa, and chlorate of potassa. Bismuthic acid prepared by either of these processes is always mixed with a certain quantity of oxide of bismuth, which may be separated by treating the substance with weak nitric acid, which dissolves the oxide of bismuth, and, when cold, does not affect the bismuthic acid. Bismuthic acid is a bright-red powder, which readily parts with a portion of its oxygen at a temperature slightly above  $212^\circ$ , and is then converted into an intermediate oxide  $\text{BiO}_4$ . Concentrated acids also decompose it, reducing it to the state of oxide  $\text{BiO}_3$ , which combines with the acid.

Bismuthic acid can combine with oxide of bismuth, and thus produce saline oxides; but these compounds have not yet been much studied. They are obtained by heating in the air a mixture of oxide of bismuth  $\text{BiO}_3$  and caustic potassa, or by passing a current of chlorine through a solution of potassa which contains oxide of bismuth in suspension. When these reactions are terminated, bismuthic acid is obtained, while, if they are prematurely arrested, brown compounds of variable proportions result, which are combinations of bismuthic acid  $\text{BiO}_5$  with oxide of bismuth  $\text{BiO}_3$ .

## SALTS FORMED BY OXIDE OF BISMUTH.

§ 995. Oxide of bismuth is a feeble base, forming with acids several crystallizable salts, which water decomposes into basic salts which are precipitated, and into very acid salts which remain in the solution.

*Nitrate of Bismuth.*

§ 996. The nitrate, which is the most important of the salts of bismuth, is obtained by dissolving bismuth in nitric acid. The liquid, when evaporated, yields large, colourless, and deliquescent crystals, of the formula  $\text{BiO}_3, 3\text{NO}_5 + 3\text{HO}$ . It dissolves without decomposition in a small quantity of water, particularly when acidulated with a few drops of nitric acid, but is decomposed if the quantity of water is greater, a white precipitate of a basic nitrate being formed, which is known by the name of *pearl powder*. This substance is used for whitening the skin, but is liable to the objection of being blackened by sulfhydryric acid. Its composition varies according to the quantity of water used in the precipitation, the temperature, and duration of contact of the basic salt with the water. Boiling water ultimately removes all its acid, and leaves only hydrated oxide.

*Sulphate of Bismuth.*

§ 997. By heating powdered bismuth with concentrated sulphuric acid, sulphurous acid is disengaged, and the metal is converted into a white, insoluble powder of sulphate of bismuth  $\text{BiO}_3, 3\text{SO}_3$ . This salt is decomposed by treatment with water into a very acid salt which remains in solution, and an insoluble bi-basic sulphate  $\text{BiO}_3, \text{SO}_3 + \text{HO}$ .

*Carbonate of Bismuth.*

§ 998. By adding carbonate of soda to an acid solution of nitrate of bismuth, a white precipitate of a basic carbonate  $\text{BiO}_3, \text{CO}_2$  is obtained, which is easily destroyed by heat, leaving a residue of oxide.

## COMPOUND OF BISMUTH WITH SULPHUR.

§ 999. Bismuth combines directly with sulphur when assisted by heat. To effect the combination, it is sufficient to heat together the two substances in the state of fine powder, a certain quantity of metallic bismuth always remaining mixed or dissolved in the sulphide. In order to obtain the latter pure, the product of the first fusion must be reduced to a fine powder, and again fused in a crucible with an additional quantity of sulphur. The sulphide then appears under the form of a gray ball, possessing a metallic lustre, and evincing in its fracture a fibrous texture. The formula of the sulphide is  $\text{BiS}_3$ . It has been found crystallized in nature, and appears to be isomorphous with the sulphide of antimony to which the same formula is assigned.

Sulphide of bismuth may be obtained by the humid way in the form of a black powder, by passing a current of sulphhydric acid through a solution of a salt of bismuth.

## COMPOUNDS OF BISMUTH WITH CHLORINE.

§ 1000. Bismuth combines directly with chlorine with disengagement of heat, and even of light, when the metal is very finely divided. If a current of chlorine be led over bismuth heated in a tubulated retort, the chloride distils over and condenses in the form of a readily fusible white substance. The same substance is obtained by distilling in a small retort a mixture of 1 part of metallic bismuth and 2 parts of bichloride of mercury. Chloride of bismuth rapidly attracts the moisture of the air, and is converted into a crystallizable hydrated chloride; which may also be obtained by dissolving metallic bismuth in aqua regia, and evaporating the liquid. Chloride of bismuth  $\text{BiCl}_3$  dissolves without change in water acidulated with chlorohydric acid, but is decomposed by fresh water; when a portion of the chloride dissolves by means of the chlorohydric acid which is set free, while a white precipitate of oxychloride of bismuth  $\text{BiCl}_3 + 2(\text{BiO}_3 + 3\text{HO})$  remains.

On pouring an acid solution of nitrate of bismuth into a solution of sea-salt, a white precipitate of very fine crystalline spangles is formed, which is an oxychloride of bismuth of the formula  $\text{BiCl}_3 + 2(\text{BiO}_3 + 3\text{HO})$ . This substance is used for whitening the skin, and is called *pearl-white*.

#### ALLOYS OF BISMUTH.

§ 1000 *bis*. By alloying bismuth with lead and tin, very fusible alloys are obtained, which are used for taking impressions, making stereotype-plates, etc. The alloy composed of 1 part of lead, 1 part of tin, and 2 of bismuth fuses at  $200^\circ$ , while that containing 5 of lead, 3 of tin, and 8 of bismuth fuses at about  $208.4^\circ$ . By diminishing the proportion of bismuth, the fusing point of the alloys obtained varies between  $212^\circ$  and  $392^\circ$ , and these substances have been used as washers for the safety-valves of the boilers of high-pressure steam-engines. Their composition was such as to fuse at a point slightly above the temperature corresponding to the maximum of tension which the steam should not exceed. When the safety-valves were out of order or overloaded, and the elastic force of the steam surpassed the maximum, the washers, by beginning to fuse, allowed the steam to escape. This means of safety was soon found to be useless, as the alloy, being kept for a long time at a temperature approaching its melting point, underwent a kind of eliquation—a more fusible alloy separated from it, and that which remained was much less fusible than the original alloy. For this reason the use of fusible washers has been abandoned.

#### DISTINCTIVE CHARACTERS OF THE SOLUBLE COMPOUNDS OF BISMUTH.

§ 1001. We have seen that all the compounds of bismuth, being soluble in a very small quantity of water, are decomposed when treated with a larger quantity, and yield white precipitates of basic salts: therefore, one of the distinctive characters of solutions of bismuth is to become cloudy when diluted with a large quantity of water.

The caustic alkalies and alkaline carbonates throw down white precipitates, insoluble in an excess of the reagent.

Sulfhydic acid and the sulfhydrates afford black precipitates, which do not redissolve in an excess of sulfhydrate.

Iron, zinc, and copper precipitate bismuth in the form of a black powder, which fuses readily on charcoal in the reducing flame of the blowpipe into a metallic globule, which becomes very brittle after cooling, and yields a powder of a characteristic rose-colour.

#### DETERMINATION OF BISMUTH; AND ITS SEPARATION FROM THE METALS PREVIOUSLY STUDIED.

§ 1002. Substances containing bismuth which are to be subjected to chemical analysis are always dissolved in nitric acid, and the

boiling liquid is precipitated by an excess of carbonate of ammonia. The precipitate is washed on the filter, and then calcined in a small porcelain capsule, in which it remains in the state of the oxide  $\text{BiO}_3$ . The calcination should not be made in a platinum crucible, because this metal is easily attacked by oxide of bismuth, especially when a small quantity of metallic bismuth can be produced by a reducing action. The filter should be calcined separately, its ashes sprinkled with a few drops of nitric acid, and then recalcined to decompose the nitrate of bismuth which is formed.

It is often necessary to precipitate bismuth in the state of sulphide by means of sulphydric acid, as, for example, when the metal exists in a liquid with other metals which are precipitated by the alkalies or alkaline carbonates, but not by sulphydric acid. It is also precipitated as sulphide when the liquid contains chlorohydric acid, because the precipitate formed by the alkaline carbonates would in this case contain chloride of bismuth, which is difficult to decompose by an excess of alkaline carbonate. The bismuth being in the state of sulphide is collected on a filter, dissolved in nitric acid, and then reprecipitated by an excess of carbonate of ammonia.

Lastly, bismuth is sometimes precipitated in the metallic state by a blade of iron or zinc, and the metallic powder, being collected on a filter, is calcined in a porcelain capsule; after which a few drops of nitric acid are added, it is recalcined, and the bismuth determined in the state of oxide.

Bismuth is easily separated by sulphydric acid passed through an acid liquid, from all the metals we have hitherto studied, with the exception of cadmium, tin, and lead. It is separated from tin by treating the sulphides, immediately after their being precipitated, with a solution of sulphhydrate of ammonia, which dissolves only the sulphide of tin. In order to separate bismuth from lead, both metals are dissolved in nitric acid, and evaporated with an excess of sulphuric acid until the vapours of the acid begin to pass over, after which they are treated with water, which dissolves only the sulphate of bismuth by means of the excess of acid. This process does not effect a very accurate separation. No method of separating bismuth from cadmium is yet known.\*

#### METALLURGY OF BISMUTH.

§ 1003. Bismuth has hitherto been found only in a small number of minerals, the only one of which sufficiently abundant and rich to be used as an ore is native bismuth, which constitutes metallic veins

\* A perfect separation of bismuth from cadmium is effected by adding a solution of cyanide of potassium to the solution of the two oxides, by which the bismuth is precipitated, while the cadmium remains in solution as a double cyanide of cadmium and potassium.

Another method might be based on the solubility of oxide of cadmium in ammonia, in which oxide of bismuth is insoluble.—*W. L. F.*

in the quartzose rocks of the old formations. All the bismuth used in the arts comes from Saxony, and is extracted by a very simple process: the ore being heated in close vessels, the bismuth fuses, separates from the gangue, and falls to the bottom of the vessel.

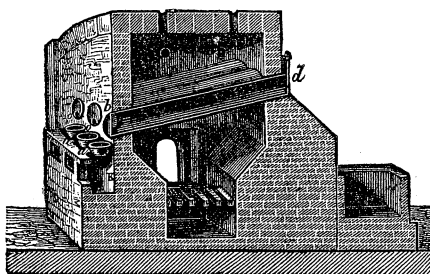


Fig. 555.

The fusion is effected in sheet-iron or cast-iron tubes *bd* (fig. 555), arranged in a furnace, and inclining downward. The ore being introduced through the opening *d*, the latter is closed, while the other end *b* is closed by a plate having a hole *o*, through which the metal escapes. It is received in earthen cups *a, a*, heated by charcoal placed in the space *K* beneath, in order to keep the metal fluid. It is then scooped out and run into moulds.

The metal thus obtained, which always contains, besides metallic sulphides and arseniurets, some foreign metals, is purified by fusion with  $\frac{1}{10}$  of its weight of saltpetre.

## ANTIMONY.

EQUIVALENT = 129 (1612.5; O = 100).

§ 1004. The antimony\* of commerce, which is rarely pure, containing most frequently a small admixture of iron, lead, arsenic, and sulphur, is purified in the laboratory by mixing it intimately with  $\frac{1}{10}$  of its weight of nitre, and fusing the mixture in an earthen crucible; when the antimony appears in the form of a metallic button, composed of very small crystalline lamellæ. The fineness of the grain of antimony is an index of its purity.

Antimony is a metal of a slightly bluish, very brilliant, silvery white colour. It fuses at  $842^{\circ}$ , and at a white-heat gives off appreciable vapours, at which temperature it may be distilled in a current of hydrogen gas; but the tension of its vapour being still very feeble, the distillation is slow. Antimony crystallizes readily from fusion, and its fracture presents very brilliant surfaces of cleavage, the disposition of which leads to the rhombohedron, and which are frequently of great extent. The tendency of the metal to crystallize may be well seen in the cakes of commercial antimony, their upper surfaces often exhibiting a beautiful star, the rays of which resemble the fern-leaf. It is a very brittle metal and easily reduced to powder in a mortar.

Antimony does not sensibly alter in the air at the ordinary temperature, while it readily oxidizes when kept in a fused state in contact with the air. Heated to a high temperature, it burns with a white flame and gives off copious fumes. If the fused metal, heated to redness, be thrown from a certain height on the floor, a very brilliant phenomenon of combustion is observed, accompanied by thick white fumes.

Finely powdered antimony dissolves in boiling concentrated chlorohydric acid, with disengagement of hydrogen gas, but does not decompose water in the presence of sulphuric acid, which will not oxidize it except when concentrated and hot, when sulphurous acid is disengaged. Nitric acid, even when dilute, readily attacks it, converting the metal into an insoluble white precipitate. Aqua regia transforms antimony into a chloride which dissolves without change in an excess of chlorohydric acid.

## COMPOUNDS OF ANTIMONY WITH OXYGEN.

§ 1005. Two well-defined compounds of antimony with oxygen are known, the quantities of oxygen contained in which are as 3 to 5.

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\* Although the ores of antimony were known to the ancients, Basil Valentine was the first who made mention of metallic antimony.



The most oxygenated compound, of which the formula is  $\text{SbO}_3$ , and which plays the part of an acid, is *antimonic acid*; while that containing the least amount of oxygen, and is expressed by the formula  $\text{SbO}_2$ , acts as a feeble base. We shall call it *sesquioxide of antimony*, or simply *oxide of antimony*.

A third oxide  $\text{SbO}_4$ , which by some chemists is regarded as an oxide *per se*, and called *antimonious acid*, should rather be considered as an antimoniate of oxide of antimony,  $\text{SbO}_3 \cdot \text{SbO}_3$ .

*Oxide of Antimony*  $\text{SbO}_2$ .

§ 1006. Oxide of antimony is formed when antimony is heated in an imperfectly closed crucible, when small elongated and very brilliant prismatic crystals, which have been called *argentine flowers of antimony*, are deposited on the sides of the crucible at a little distance above the fused metal. But as it is difficult to prevent the oxide prepared in this way from containing some antimoniate of oxide of antimony, a better method of obtaining the oxide in a state of purity consists in pouring, by small quantities at a time, a solution of chloride of antimony  $\text{SbCl}_3$  into a boiling solution of carbonate of soda; when the oxide of antimony separates in the form of small crystals.

Oxide of antimony, the colour of which is a grayish white, fuses at a red-heat, and sublimes at a higher temperature. It readily absorbs oxygen when heated in the air, and is converted into antimoniate of oxide of antimony, while it is indecomposable by heat alone, but is easily reduced by hydrogen or by charcoal.

The oxide of antimony, precipitated when cold from the solution of the chloride by carbonate of soda, which is hydrated, and has the formula  $\text{SbO}_3 + \text{HO}$ , dissolves readily in alkaline liquids, forming true salts in which it acts the part of an acid.

Oxide of antimony contains:

Antimony .....	84.31
Oxygen .....	15.69
	<hr/>
	100.00

Its formula is written  $\text{SbO}_2$ ; and consequently the equivalent of antimony is obtained from the proportion:

$$15.68 : 84.32 :: 24 : x, \text{ whence } x=129.$$

*Antimonic Acid*  $\text{SbO}_3$ .

§ 1007. Antimonic acid is obtained by attacking antimony by nitric acid, or better still, by aqua regia containing an excess of nitric acid, when an insoluble white powder of hydrated antimonic acid is formed, which loses its water at a slightly elevated temperature, and is converted into anhydrous antimonic acid. The hydrated acid is also obtained by decomposing the perchloride of

antimony  $\text{SbCl}_5$  by water; but the hydrates obtained by these two processes are far from being identical. Their capabilities of saturation with bases being different, they in this respect exhibit a phenomenon analogous to that observed in stannic acid, and which was treated of (§ 479 *et seq.*) when speaking of phosphoric acid, which presents the same feature. The product obtained by attacking antimony by nitric acid, and to which the name of *antimonic acid* has been preserved, only saturates 1 equivalent of a base, producing neutral salts of the general formula  $\text{RO},\text{SbO}_5$ ; while the precipitate obtained by decomposing perchloride of antimony by water saturates 2 equiv. of a base, and forms neutral salts of the formula  $2 \text{RO},\text{SbO}_5$ . It has been called *metantimonic acid*.

Anhydrous antimonic acid is a powder of a yellowish-white colour, which is decomposed by a red-heat, producing antimoniate of oxide of antimony  $\text{SbO}_3,\text{SbO}_5$ .

The *neutral antimoniate of potassa* is prepared by heating in an earthen crucible 1 part of metallic antimony and 4 parts of nitrate of potassa, and treating the powdered mass with a small quantity of tepid water, which dissolves the potassa in excess and the undecomposed nitrite of potassa. The residue is then boiled with water for several hours, by which the anhydrous antimoniate of potassa, which is insoluble, is converted into a soluble hydrated antimoniate. An insoluble residue remains, which is the *bi-antimoniate of potassa*  $\text{KO},2\text{SbO}_5$ ; and the liquid leaves after evaporation a gummy mass which presents no appearance of crystallization, and the formula of which, when desiccated in dry air, is  $\text{KO},\text{SbO}_5+5\text{HO}$ . This neutral antimoniate  $\text{KO},\text{SbO}_5+5\text{HO}$  is converted into a crystalline powder of bi-antimoniate  $\text{KO},2\text{SbO}_5$  by passing a current of carbonic acid through its solution.

By heating in a silver crucible antimonic acid or neutral antimoniate of potassa with a large excess of potassa, a fused mass which completely dissolves in a small quantity of cold water is obtained; and the solution, when evaporated in vacuo, deposits small crystals of *metantimoniate of potassa*  $2\text{KO},\text{SbO}_5$ . This salt dissolves, without apparent decomposition, in a small quantity of cold water to which a certain quantity of caustic potassa has been added, while it is decomposed by pure water into potassa and *acid metaantimoniate of potassa*  $\text{KO},\text{SbO}_5+7\text{HO}$ , which is but slightly soluble in cold water. Water dissolves it more freely at a temperature of  $105^\circ$  or  $120^\circ$ , while a prolonged contact with cold water transforms it into neutral antimoniate of potassa; which transformation is rapidly effected by boiling the liquid. The solution of the acid metantimoniate of potassa possesses the property of precipitating the salts of soda, and yielding an acid metantimoniate of soda, which is almost insoluble in water. It is the only reagent as yet known which precipitates soda from its solutions; but it is necessary to use freshly prepared acid metantimoniate of potassa, as the salt

is after some time converted into the common antimoniate, which does not precipitate the salts of soda.

*Antimoniate of Oxide of Antimony*  $\text{SbO}_3, \text{SbO}_5$ .

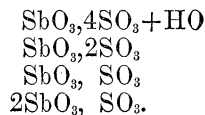
§ 1008. By heating antimonie acid until oxygen is no longer given off, a white powder, of which the composition is  $\text{SbO}_4$ , but which should be written  $\text{SbO}_4, \text{SbO}_5$ , remains. This product, which is sometimes called *antimonious acid*, is also formed when antimony is roasted in the open air. A solution of tartaric acid or bi-tartrate of potassa abstracts its oxide of antimony, leaving the antimonie acid, while a solution of caustic potassa dissolves, on the contrary, the antimonie acid, and leaves the oxide of antimony; which reactions render the existence of both oxide of antimony and antimonie acid in this body very probable. Antimoniate of oxide of antimony is infusible.

SALTS FORMED BY OXIDE OF ANTIMONY.

§ 1009. Oxide of antimony  $\text{SbO}_3$  is a feeble base, which nevertheless forms several salts with acids.

A nitrate of antimony is obtained by treating cold antimony with fuming nitric acid, in the shape of crystalline spangles of the formula  $2\text{SbO}_3, \text{NO}_5$ . The salt is decomposed by water, and transformed into hydrated oxide of antimony.

Several compounds of oxide of antimony with sulphuric acid are known, and present the following composition:



We do not find among these salts the compound  $\text{SbO}_3, 3\text{SO}_3$ , which should be regarded as the neutral sulphate of antimony, from the formula  $\text{SbO}_3$  which we have adopted to represent oxide of antimony.

The oxychloride of antimony  $\text{SbCl}_3, 2\text{SbO}_3 + \text{HO}$ , the preparation of which will be explained hereafter, is converted into the sulphate  $\text{SbO}_3, 4\text{SO}_3 + \text{HO}$  when it is treated with concentrated sulphuric acid, while the sulphate  $\text{SbO}_3, 2\text{SO}_3$  is obtained by treating oxide of antimony with fuming oil of vitriol, (Nordhausen sulphuric acid.) Lastly, the sulphate  $\text{SbO}_3, 4\text{SO}_3 + \text{HO}$  is decomposed by treatment with hot water, leaving a residue of the formula  $2\text{SbO}_3, \text{SO}_3$ .

COMPOUND OF ANTIMONY WITH HYDROGEN.

§ 1010. Antimony forms a gaseous compound with hydrogen, which resembles in its composition that of arseniuretted hydrogen and phosphuretted hydrogen gas, but which hitherto has not been

obtained in a state of purity. By introducing a solution of protochloride of antimony into a bottle in which hydrogen is being disengaged by the reaction of dilute sulphuric acid on zinc, the hydrogen always contains a certain quantity of antimoniuiretted hydrogen gas, which is easily recognised on igniting the gas, when it burns with a yellowish flame which evolves white fumes, and which, on being allowed to play on a cold porcelain capsule, yields glittering spots of metallic antimony. If the gas be passed through a heated tube, a brilliant ring of metallic antimony forms on the sides of the tube, in front of the heated portion.

#### COMPOUNDS OF ANTIMONY WITH SULPHUR.

§ 1011. Two combinations of antimony with sulphur are known; and while the formula of the first, which we shall call *sulphide of antimony*, is  $\text{SbS}_3$ , corresponding to the oxide  $\text{SbO}_3$ , the second corresponds to antimonic acid, and its formula being  $\text{SbS}_5$ , we shall call it *sulfantimonic acid*.

Sulphide of antimony is found in nature, and is the only ore of antimony. It always occurs crystallized, but the prismatic crystals are so dovetailed into each other, that it is often difficult to ascertain their form. It is sometimes found in isolated crystals, which are prisms belonging to the fourth system. Sulphide of antimony, which is of a deep gray colour, and a very decided metallic lustre, fuses below a red-heat, and readily crystallizes on cooling from a white-heat. It exhales copious fumes, and may be distilled in a current of nitrogen gas. Its density is 4.62. The sulphide is formed by the direct combination of antimony with sulphur, by several successive fusions, when a purer sulphide than that occurring in nature is obtained, which always contains a small quantity of other metallic sulphides.

Sulphide of antimony is easily roasted in the air, during which operation no sulphate is formed, but only oxide of antimony, which combines with the undecomposed sulphide, especially under the influence of an elevated temperature. Fusible oxysulphides are thus formed, which, after cooling, yield brown vitreous substances, called in commerce *glass of antimony*, *liver of antimony*, or *crocus*, according to the proportions of the substances entering into their composition. Glass of antimony, which contains about 8 parts of oxide and 1 of sulphide, is transparent and of a reddish-yellow colour, while crocus, which contains 8 parts of oxide and 2 of sulphide, is opaque and reddish yellow. Liver of antimony is opaque and of a deep brown colour, and contains nearly 4 parts of sulphide for 8 of oxide.

Hydrogen decomposes sulphide of antimony at a red-heat with disengagement of sulphhydric acid, while the antimony remains in the metallic state; but it is difficult to prevent a small quantity of antimony from being disengaged in the state of antimoniuiretted

hydrogen gas. Charcoal also decomposes sulphide of antimony at a high temperature, while sulphide of carbon is disengaged, and the antimony remains in the metallic state. It is, however, difficult by these methods to obtain antimony entirely free from sulphur.

Iron, zinc, and copper decompose sulphide of antimony at a red-heat; but the metallic antimony thus obtained always contains a certain quantity of these metals. Concentrated chlorohydric acid readily dissolves sulphide of antimony with disengagement of sulphydric acid, which reaction is sometimes applied in the laboratory to the preparation of sulphydric acid (§ 149). Boiling concentrated sulphuric acid attacks sulphide of antimony and evolves sulphurous acid. Nitric acid converts it into an insoluble oxide of antimony and sulphuric acid.

The alkalies and alkaline carbonates decompose sulphide of antimony both in the dry and humid way, sulphide of antimony and a compound of oxide of antimony with potassa being formed. When the sulphide of antimony is in excess, there is formed in addition a compound of sulphide of antimony with monosulphide of potassium, in which combination the sulphide of antimony acts the part of an acid. If the decomposition be effected in a brasqued crucible, a portion of the antimony separates in the metallic state.

The sulphide of antimony  $\text{SbS}_3$  may be prepared in the humid way, by passing a current of sulphydric acid gas through a solution of chloride of antimony  $\text{SbCl}_3$  in water charged with chlorohydric acid, when an orange-coloured precipitate of *hydrated sulphide* is formed, which dissolves readily in the alkaline sulphurets, when it plays the part of an acid. Acids precipitate anew the hydrated sulphide from solutions of the sulphosalts. Heat easily drives off the water from the hydrated sulphide, which then is converted into a gray anhydrous sulphide.

In medicine the hydrated sulphide is used either mixed or combined with oxide of antimony, and often with sulfantimonic acid  $\text{SbS}_5$ , and is known by the name of *kermes mineral*, *golden sulphide of antimony*, etc.

Kermes is prepared either in the dry or humid way.

In the former case, a mixture of 5 parts of native sulphide of antimony and 3 parts of dried carbonate of soda is fused in an earthen crucible, and the fused substance, after being reduced to powder, is boiled with a large quantity of water. The hot liquid is rapidly filtered, taking care that it does not cool in the filter; when the liquid, which is nearly colourless, or but slightly yellow, deposits on cooling a copious brown flaky precipitate, which is the kermes. It should be quickly washed, dried at a low temperature, and kept in well-stoppered bottles.

It is obtained in the humid way by boiling 1 part of native sulphide of antimony, finely powdered, with 20 or 25 parts of dried

carbonate of soda, and 250 parts of water; the liquid, which is almost colourless, depositing the kermes on cooling.

By pouring chlorohydric acid into the mother liquid from which the kermes has been deposited, a precipitate of a deeper red colour than the precipitate is obtained, which has been called the *golden sulphide*. It is a mixture of sulphide of antimony  $\text{SbS}_3$ , sulfantimonic acid  $\text{SbS}_5$ , and oxide of antimony  $\text{SbO}_3$ .

It is easy to ascertain that the oxide of antimony exists only as an admixture in kermes mineral and in the golden sulphide; an examination with the microscope shows the oxide of antimony in the form of white points scattered through the mass.

Kermes contains, also, a small quantity of sulphide of potassium combined with the oxide, or with a portion of the sulphide of antimony.

*Sulfantimonic acid*  $\text{SbS}_5$  is obtained by passing a current of sulphydric acid through a solution of perchloride of antimony  $\text{SbCl}_5$  in dilute chlorohydric acid, when a yellow precipitate is formed, readily dissolving in the alkaline sulphides, and forming sulphosalts which frequently crystallize with great facility. For medicinal purposes, a *sulfantimoniate of sodium* is often prepared by mixing intimately 18 parts of very finely powdered sulphide of antimony, 12 parts of dried carbonate of soda, 13 of lime and  $3\frac{1}{4}$  of sulphur, and allowing the mixture, after it has been triturated for a long time, to digest for several days in a flask filled with water, the vessel being frequently shaken. The liquid, when evaporated, first by heat, and then under the receiver of an air-pump, yields large crystals of a pale yellow colour, and of which the formula is  $3\text{NaS}, \text{SbS}_5 + 18\text{HO}$ .

#### COMPOUNDS OF ANTIMONY WITH CHLORINE.

§ 1012. Antimony forms two compounds with chlorine,  $\text{SbCl}_3$  and  $\text{SbCl}_5$ , corresponding to the oxide of antimony  $\text{SbO}_3$  and antimonie acid  $\text{SbO}_5$ .

The chloride of antimony  $\text{SbCl}_3$  is obtained by passing chlorine slowly through a tube containing antimony in excess, while the perchloride  $\text{SbCl}_5$  would be formed if the chlorine be in too great quantity. The chloride is also obtained by distilling in a glass retort an intimate mixture of 1 part of antimony and 2 parts of bichloride of mercury; but the most economical method of preparing it consists in dissolving native sulphide of antimony in chlorohydric acid, and evaporating the liquid with an excess of acid. In the laboratory the residue of the preparation of sulphydric acid is used for this purpose.

Chloride of antimony  $\text{SbCl}_3$  is a white, readily fusible substance, which, from its consistence at the ordinary temperature, was formerly called *butter of antimony*. It volatilizes at a temperature below a red-heat.

VOL. II.—T

The protochloride of antimony is deliquescent in a moist atmosphere, and dissolves without change in a small quantity of water, while the addition of chlorohydric acid is necessary for its solution in larger quantities of the same liquid; as with much pure water decomposition would ensue, a white soluble powder of an oxychloride of antimony  $\text{SbCl}_3 \cdot 2\text{SbO}_3 + \text{HO}$ , called by the old chemists *powder of Algaroth*, being formed. By treating a chlorohydric solution of chloride of antimony with hot water, the clear liquid deposits, on cooling, crystals of another oxychloride of the formula  $\text{SbCl}_3 \cdot 5\text{SbO}_3$ . Repeated washings decompose the oxychlorides of antimony and leave pure oxide. The best method of preventing solutions of chloride of antimony from being clouded by water consists in the addition of a certain quantity of tartaric acid.

Anhydrous chloride of antimony combines with dry ammoniacal gas, yielding a compound of which the formula is  $\text{NH}_3 \cdot \text{SbCl}_3$ . With the alkaline chlorides and chlorohydrate of ammonia it forms double crystallizable chlorides.

In surgery, chloride of antimony is used to cauterize wounds. Gunsmiths employ it for bronzing gun-barrels, the iron of which, being thus covered with a very thin pellicle of metallic antimony, is preserved from rust.

*Perchloride of antimony*  $\text{SbCl}_5$  is prepared by heating antimony in a current of dry chlorine, the same apparatus being used as that employed for the preparation of the perchloride of tin. The liquid collected in the receiver, which always contains some protochloride  $\text{SbCl}_3$  in solution, must be completely saturated with chlorine, and then distilled in a small retort. The first portions which pass over contain a considerable quantity of dissolved chlorine, and are coloured deeply yellow, while the subsequent liquid, being nearly colourless, is collected by itself. Perchloride of antimony nevertheless appears to decompose at the temperature of its ebullition under the ordinary pressure of the atmosphere, as it always disengages chlorine when subjected to distillation.

#### DISTINCTIVE CHARACTERS OF THE SOLUBLE COMPOUNDS OF ANTIMONY.

§ 1013. The characteristic reactions of solutions of antimony which we are about to indicate refer to the protochloride of antimony and to *emetic tartar*, which is a double tartrate of antimony and potassa. They will serve to distinguish antimony in all cases, because it is always easy to convert its other compounds into these two products.

Solutions of antimony produce with potassa and soda white precipitates, which are easily redissolved in an excess of alkali. Ammonia throws down a white precipitate insoluble in an excess of the reagent.

The alkaline carbonates yield, carbonic acid being at the same

time evolved, a white precipitate of the hydrated oxide, which does not dissolve in an excess of carbonate.

Sulfhydic acid and sulfhydrate of ammonia yield a characteristic orange-coloured precipitate, which dissolves in an excess of sulfhydrate.

A blade of iron or zinc precipitates antimony in the form of a black powder, from which, by fusion on charcoal before the blow-pipe, metallic antimony is obtained, possessing the characteristic physical properties which distinguish it from tin, this metal being analogous to it in its chemical reactions.

#### DETERMINATION OF ANTIMONY; AND ITS SEPARATION FROM THE METALS PREVIOUSLY STUDIED.

§ 1014. Antimony can neither be determined as the oxide  $\text{SbO}_3$ , nor as antimonious acid  $\text{SbO}_2$ , as the purity of these substances would always be questionable. It is precipitated from its solution by sulfhydic acid, a sufficient quantity of chlorohydric acid being added to prevent the liquid from being clouded by water, or still better, tartaric acid, when the addition of this substance does not interfere with the determination of the remaining substances. The liquid, after being saturated with sulfhydic acid gas, is exposed to a gentle heat for several hours in an imperfectly closed bottle, in order to allow the greater portion of the sulfhydic acid to be disengaged; when the precipitate of sulphide of antimony is collected on a filter, and, after being well washed, is dried on the filter at a temperature of  $212^\circ$ . The filter, with the substance it contains, being weighed, the latter is separated as completely as possible, and dropped into a small flask; when the weight of the filter, subtracted from that of the filter and substance together, gives the weight of the sulphide. The small quantity which always remains in the pores of the filter can be taken into account by incinerating the paper and considering the residue as antimoniate of antimony  $\text{SbO}_3, \text{SbO}_2$ . The sulphide of antimony being now treated with hot aqua regia, the antimony dissolves as perchloride, and the sulphur in the state of sulphuric acid, the oxidation of the sulphur being accelerated by an addition of a small quantity of chlorate of potassa. Chloride of barium is then poured into the liquid properly diluted with water, while a small quantity of tartaric acid is added to prevent the precipitation of oxychloride of antimony; when sulphate of baryta is precipitated and weighed after calcination. By subtracting from the weight of the sulphide of antimony the weight of sulphur corresponding to the sulphate of baryta, the weight of the metallic antimony is obtained.\*

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\* The method given in the text may be considerably shortened, by collecting the sulphide of antimony on a weighed filter, which has been previously dried at  $212^\circ$ , (a balanced filter;) when the weight of the filter with the precipitate, after being dried at the same temperature, minus the weight of the filter, gives imme-



The sulphide of antimony may also be heated in a current of hydrogen gas, when metallic antimony remains, sulphydric acid and vapour of sulphur being disengaged. For this purpose, the sulphide of antimony is placed in a small porcelain crucible, through the lid of which a tube passes conveying dry hydrogen to the bottom of the crucible, and, the temperature being gradually raised, the reaction is maintained until the crucible no longer alters in weight.

In no case can antimony be weighed in the state of sulphide, its composition always being a matter of uncertainty.

§ 1015. In order to separate antimony from the metals we have previously studied, the insolubility of antimonic acid in nitric acid is sometimes relied on, and sometimes its precipitation by sulphydric acid, and the solubility of sulphide of antimony in alkaline sulphhydrates. Antimonic acid not being absolutely insoluble in nitric acid, it is always necessary to test for antimony in the liquid by means of sulphydric acid.

In order to separate antimony from the alkaline, alkalino-earthly, and earthy metals, chlorohydric acid is added to the liquid to prevent the deposit of oxychloride of antimony, and sulphydric acid gas is passed through it. When the antimony is nearly wholly precipitated, the liquid is diluted with water, because sulphide of antimony is slightly soluble in chlorohydric acid, unless the latter is very dilute; and sulphydric acid is again passed through it. The precipitate of sulphide of antimony having been separated on a filter, the substances remaining in solution may be determined by the ordinary processes.

Antimony is separated from manganese, iron, chrome, cobalt, nickel, and zinc by passing sulphydric acid through the liquid acidulated with chlorohydric acid. The precipitation of oxychloride of antimony is frequently prevented by the addition of tartaric acid, in which case, however, the other metals can no longer be completely separated from their solutions either by ammonia or the alkaline carbonates, because tartaric acid prevents their precipitation. The liquid then being saturated with ammonia, the metals are precipitated by sulphhydrate of ammonia.

Antimony is separated from cadmium, lead, and bismuth by saturating the chlorohydric solution with ammonia, and adding a large excess of sulphhydrate of ammonia in which a certain quantity of sulphur has been dissolved. The bottle, imperfectly closed, is exposed for several hours to a temperature of from  $120^{\circ}$  to  $140^{\circ}$ ; when the antimony dissolves in the state of sulphide, while the sulphides of the other metals are precipitated. By decomposing the

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directly the weight of all the antimony as sulphide  $SbS_3$ , whence that of the metallic antimony may be deduced. The antimony having been in the state of protochloride  $SbCl_3$ , is precipitated entirely as protosulphide  $SbS_3$ , in all cases when the antimonic compound has not been dissolved in nitromuriatic acid.—*W. L. F.*

filtered liquid by dilute chlorohydric acid, the sulphide of antimony separates, mixed with a large quantity of free sulphur.

Antimony cannot be separated from tin by any of the processes just described. The reactions of these metals being very similar, their separation is consequently a matter of some difficulty. Both metals being dissolved in aqua regia, are precipitated together by a blade of zinc, and the metallic precipitate is weighed. It is then dissolved in aqua regia with an excess of chlorohydric acid, and a blade of tin dipped into the liquid when properly diluted, by which the antimony alone is precipitated, and perfectly, if care be taken to keep the liquid gently heated, with a slight excess of chlorohydric acid.

#### DETECTION OF ANTIMONY IN CASES OF POISONING.

§ 1016. As compounds of antimony act as poisons on the animal economy, it occasionally falls to the lot of the medical man to investigate their toxicological effects, the subject of investigation being sometimes food and sometimes portions of the human body. For this purpose, the suspected matter being diluted with water, a certain quantity of pure chlorohydric acid added, and the liquid boiled, 20 gm. of chlorate of potassa for every 100 parts of matter are thrown into it by small quantities at a time, the liquid is filtered while boiling, and concentrated by evaporation. It is then introduced into a Marsh's apparatus, as represented in fig. 260; when a glittering ring of metallic antimony forms in the tube *fg*, in which all the characteristic reactions of antimony may be observed. A blade of tin may also be plunged into the filtered liquid after it has been properly concentrated, when the antimony is deposited on the tin. The tin is dissolved in aqua regia, with the black precipitate which may have separated from it, after which it is evaporated with an excess of chlorohydric acid, redissolved with the same acid in a very dilute state, and the solution treated, as before, in Marsh's apparatus.

#### ALLOYS OF ANTIMONY.

§ 1017. Although antimony combines with a great number of metals, the only alloys used in the arts are those of antimony and lead for printers' types, and those of antimony and tin for various purposes.

Antimony combines readily with potassium and sodium, producing alloys which decompose water at the ordinary temperature with disengagement of hydrogen gas, and which frequently detonate suddenly when moistened with a small quantity of water or exposed to a damp atmosphere. An alloy of antimony and fused potassium is prepared by heating for several hours, in an earthen crucible, a mixture of 6 parts of tartar emetic and 1 of nitre, or equal parts of metallic antimony and black flux; when the metallic button

found at the bottom of the crucible will decompose water at the ordinary temperature, with disengagement of hydrogen. A finely divided alloy, which explodes when moistened with a drop of water, is obtained by heating for several hours in an earthen crucible, at a high temperature, 100 parts of tartar emetic and 3 parts of lamp-black. The crucible should be placed, after the calcination, under a well-dried bell-glass, which should be removed only when it is perfectly cool. This substance requires the most careful handling, as it frequently gives rise to fearful accidents by detonating spontaneously.

By fusing in an earthen crucible, at a strong white-heat, a mixture of 70 parts of metallic antimony and 30 of iron-filings, a very hard metallic globule is obtained, which on being filed emits sparks of fire. This substance is known, in the laboratory, under the name of *Réaumur's alloy*.

#### METALLURGY OF ANTIMONY.

§ 1018. We have said that the sulphide is the only ore of antimony. It is first separated from its gangue by simple fusion, for which purpose the ore is placed in large crucibles P (fig. 556), arranged in two rows in a furnace.

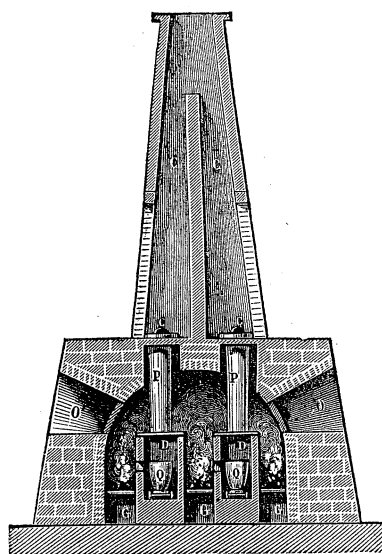


Fig. 556.

Each crucible has, at its lower part, an aperture corresponding to an opening made in the benches on which it rests. Under the crucibles, and in the compartments D of the furnace, are earthen pots Q, in which the fused antimony is collected, while pine wood is burned on the grates G. Sometimes the ore is heated in a reverberatory furnace, when the fused sulphide runs into a cavity in the hearth, and flows outwardly into iron pots.

The sulphide of antimony is then roasted in a reverberatory furnace, where it is converted into oxysulphide or glass of antimony; after which the roasted substance is pulverized, and then

mixed with 20 per cent. of charcoal soaked in a strong solution of carbonate of soda. This mixture being calcined in crucibles, the oxide of antimony is reduced to the metallic state, while a portion of the sulphide is decomposed by the carbonate of soda and yields an additional quantity of metal. A globule of antimony, called

*regulus of antimony*, is found at the bottom of the crucibles, surmounted by an alkaline dross containing sulphide and oxide of antimony, and which may be used for the preparation of kermes mineral.

Metallic antimony may also be obtained by decomposing sulphide of antimony by iron; but its quality is then inferior, as it contains a large proportion of iron; and although the latter may be separated by subjecting the substance to a partial roasting, a considerable quantity of antimony must be oxidized in order to effect a complete separation of the iron.

## URANIUM.

EQUIVALENT = 60 (750.0; O = 100).

§ 1019. Uranium\* is prepared in the same way as magnesium; that is, by decomposing its chloride by means of potassium, for which purpose a mixture of about 2 parts of protochloride of uranium and 1 of potassium is gently heated in a platinum crucible, the lid of which is fastened down by iron wire. When the reaction, which ensues with lively incandescence, is terminated, the crucible is again heated in order to volatilize the greater portion of the potassium in excess, after which the crucible is allowed to cool, and the substance treated with water, which, dissolving the chloride of potassium, leaves the uranium in the form of a black powder. Small plates of uranium are often found on the sides of the crucible, in which case the metal possesses a lustre resembling that of silver, and a certain degree of malleability.

Uranium is very combustible: it ignites in the air when heated above  $392^{\circ}$ , burning with great brilliancy, and being transformed into a deep-green oxide. It remains unchanged in the air at the ordinary temperature, and does not decompose cold water. It dissolves with disengagement of hydrogen in the dilute acids, and produces green solutions. It unites with chlorine with great disengagement of heat and light, forming a green volatile chloride. With sulphur it combines directly, and at a low temperature.

## COMPOUNDS OF URANIUM WITH OXYGEN.

§ 1020. Two compounds of uranium with oxygen are known:

A protoxide  $\text{UO}$ ;

A sesquioxide  $\text{U}_2\text{O}_3$ .

Several intermediate oxides, which are regarded as compounds of the first two, are also known.

*Protoxide of uranium*  $\text{UO}$  is prepared by decomposing the sesquioxalate of uranium  $\text{U}_2\text{O}_3 \cdot \text{C}_2\text{O}_3$  by hydrogen at a red-heat, when a brown powder remains, which must be preserved in an atmosphere of hydrogen, by hermetically sealing the ends of the tube in which the decomposition has been effected. The oxide is very pyrophoric, becoming feebly incandescent in the air, and being converted into a black powder, which is an intermediate oxide  $\text{U}_4\text{O}_9$ , and the formula of which should probably be written  $2\text{UO} \cdot \text{U}_2\text{O}_3$ . The protoxide is obtained in a more aggregated form by decomposing the

\* Oxide of uranium was discovered in 1789, by Klaproth; while metallic uranium was isolated by M. Pélégot only as late as 1842.

double chloride of uranium and potassium by hydrogen, when the protoxide of uranium remains, after treatment with water, in the form of crystalline spangles which do not change in the air at the ordinary temperature.

Protoxide of uranium may also be obtained in the hydrated state by decomposing by ammonia the green solution of protochloride of uranium  $\text{UCl}$ ; a flaky, reddish-brown precipitate being formed, which readily dissolves in acids.

By heating protoxide of uranium in the air to a dull red-heat, it is converted into an oxide of a deep olive colour and a velvety appearance, the composition of which is  $\text{U}_3\text{O}_4$ , or more probably,  $\text{UO}, \text{U}_2\text{O}_3$ , as by solution in acids a protosalt and a sesquisalt are formed. At a higher temperature this oxide is decomposed and changed into a black oxide  $2\text{UO}, \text{U}_3\text{O}_3$ . The oxide of uranium has been long regarded as a metal, and called *uranium*.

Sesquioxide of uranium  $\text{U}_2\text{O}_3$ , which is the base of the yellow salts of uranium, has not yet been isolated. When the sesquinitrate is decomposed by a properly regulated heat, an orange-coloured basic salt is first obtained, while on still increasing the temperature it loses a portion of its oxygen, while it at the same time parts with the last traces of its acid. By precipitating a solution of a yellow salt of uranium by potassa or ammonia, a yellow precipitate is formed, which is a true uranate of the base which effected the precipitation. Hydrated sesquioxide of uranium is prepared as follows:—A solution of the yellow oxalate of uranium is exposed to the action of solar heat, which effects the disengagement of a mixture of carbonic acid and oxide, while a flaky precipitate of a violet-brown colour is formed. The precipitate rapidly absorbs the oxygen of the air while it is being collected on a filter, and is converted into a yellow substance, which is the hydrated sesquioxide  $\text{U}_2\text{O}_3 + 2\text{HO}$ .

#### PROTOSALTS OF URANIUM.

§ 1021. Only a small number of protosalts of uranium are known, from the solutions of which ammonia and the alkalies throw down brownish black precipitates, which turn yellow by exposure to the air, being then converted into sesquioxide, which remains in combination with the alkali. Sulfhydic acid exerts no action on these salts, while the sulfhydrates yield black precipitates. The green salts of the protoxide of uranium are readily converted into yellow salts of the sesquioxide by oxidizing reagents; and nitric acid or chlorine effect the same change, even when cold.

*Protosulphate of uranium* is prepared by pouring sulphuric acid into a concentrated solution of green protochloride, heat being applied to drive off the chlorohydric acid. By treatment with water a liquid is obtained which deposits green crystals of the protosulphate, of which the formula is  $\text{UO}, \text{SO}_3 + 4\text{HO}$ .

By adding oxalic acid to a solution of the green protochloride, a greenish-white precipitate is obtained, which may be washed in boiling water without dissolving, and consists of protoxalate of uranium, with the formula  $\text{UO}, \text{C}_2\text{O}_3 + 3\text{HO}$ .

#### SESQUISALTS OF URANIUM.

§ 1022. The sesquioxide of uranium  $\text{U}_2\text{O}_3$  forms a great number of crystallizable salts, the peculiarity of whose composition distinguishes them from salts formed by the other metallic sesquioxides. We have seen that, in all the neutral salts formed by a same acid, the ratio between the oxygen of the base and that of the acid is constant; being as 3:1 for the sulphates: the formula of the neutral sulphates are therefore  $\text{RO}, \text{SO}_3$  for the protoxides, and  $\text{R}_2\text{O}_3, 3\text{SO}_3$  for the sesquioxides. The ratio being as 5:1 for the nitrates,  $\text{RO}, \text{NO}_5$  is the formula of the protonitrates, and  $\text{R}_2\text{O}_3, 3\text{NO}_5$  that of the sesquinitrates. But, when the sulphate, or nitrate, of the sesquioxide of uranium is crystallized in any excess whatever of its respective acid, the crystallized salts always present the formula  $\text{U}_2\text{O}_3, \text{SO}_3$  and  $\text{U}_2\text{O}_3, \text{NO}_5$ . If, therefore, we admitted the general application of the law of composition of salts first laid down, these salts would be tri-basic salts, which would be very remarkable, inasmuch as they have crystallized in presence of a great excess of acid. In order to remove this anomaly, several chemists have supposed the sesquioxide of uranium to be a true protoxide, formed by the combination of one equivalent of oxygen with an already oxidized radical, which would present the composition of protoxide of uranium, and which they call *uranyle*. Sesquioxide of uranium being therefore, in their opinion, a *protoxide of uranyle*, they write its formula  $(2\text{UO})\text{O}$ , and the salts of the sesquioxide of uranium are *neutral salts of protoxide of uranyle*  $(2\text{UO})\text{O}, \text{SO}_3, (2\text{UO})\text{O}, \text{NO}_5$ , etc. etc. We shall have occasion to meet with several other compounds of uranium which may be cited in favour of this opinion.

Solutions of the sesquisalts of uranium, or protosalts of uranyle, are of a beautiful yellow colour, and throw down with the alkalies yellow precipitates of *uranates*, in which the sesquioxide of uranium acts the part of a weak acid with powerful bases. The alkaline carbonates and carbonate of ammonia throw down granular yellow precipitates, which are double carbonates and dissolve in an excess of the reagent. Sulfhydric acid exerts no action on solutions of sesquisalts of uranium, while the sulfhydrates yield a brownish-yellow precipitate. Prussiate of potash gives a brownish-red precipitate.

*Sesquinitrate of uranium*, which is the most important of all the salts of this metal, is obtained directly from the ore of uranium. The principal minerals containing uranium are *pitchblende* and *uranite*. Pitchblende, which chiefly consists of oxide of uranium  $\text{UO}, \text{U}_2\text{O}_3$ , and forms compact black masses, with a brilliant frac-

ture, resembling pitch, occurs principally in Bohemia; while uranite, which is a double phosphate of the sesquioxide of uranium and lime ( $\text{CaO}, 2\text{U}_2\text{O}_3, \text{PhO}_5 + 8\text{HO}$ ), and forms yellow crystalline lamellæ, with greenish reflections, is found in most abundance in the environs of Autun.

Bohemian pitchblende is the material which is always used for the preparation of the compounds of uranium. The mineral, being reduced to a fine powder, is levigated to separate the lighter earthy matter, and then treated with nitric acid, which readily attacks it; after which the solution is evaporated to dryness and treated with water, which leaves undissolved a brick-red residue, consisting of sulphate of lead and sesquioxide of iron combined with a certain quantity of arsenious acid; while the liquid, which is of a greenish-yellow colour, affords after suitable evaporation a copious and confused crystallization of sesquinitrate of uranium. The sirupy mother liquid is decanted, and the crystals, after having been allowed to drain, are redissolved in water for the purpose of recrystallization. As the mother liquid still contains a considerable quantity of sesquinitrate of uranium which cannot crystallize on account of the presence of foreign salts, it is diluted with water, and treated with a current of sulphydric acid gas to precipitate the sulphides of copper, lead, and arsenic, after which the filtered liquid is again evaporated to dryness and treated with cold water, when a ferruginous deposit remains. The liquid then yields on evaporation an additional quantity of crystallized sesquinitrate of uranium.

The nitrate of uranium thus prepared undergoes a last purification by being placed in a flask with ether, in which it is considerably soluble, and from which, by evaporation of the ether, pure nitrate of uranium is deposited, which, after being redissolved in water, is again crystallized.

Sesquinitrate of uranium forms beautiful, often very large, yellow crystals, which exhibit green reflections, like nearly all the sesquisalts of uranium. Its formula is  $\text{U}_2\text{O}_3, \text{NO}_5 + 6\text{HO}$ , or  $(2\text{UO})\text{O}, \text{NO}_5 + 6\text{HO}$ . It melts in its water of crystallization, with which it parts nearly wholly, yielding a crystalline mass after cooling. This salt is used for the preparation of all the other compounds of uranium: calcination converts it into oxide.

*Sesquisulphate of uranium*, which is prepared by decomposing the nitrate by sulphuric acid, forms several crystallizable double sulphates. The formula of the double sulphate of uranium and potassa is  $\text{U}_2\text{O}_3, \text{SO}_3 + \text{KO}, \text{SO}_3 + 2\text{HO}$ , and will be seen to possess no analogy with the alums.

*Sesquioxalate of uranium*, being but slightly soluble in water, is precipitated when oxalic acid is poured into a solution of the sesquinitrate. The formula of the salt is  $\text{U}_2\text{O}_3, \text{C}_2\text{O}_3 + 3\text{HO}$ , which should be written  $(2\text{UO})\text{O}, \text{C}_2\text{O}_3 + 3\text{HO}$ , if the hypothesis of uranyle be admitted.



Sesquioxide of uranium communicates a clear yellow colour with beautiful green reflections to vitreous fluxes, and has been used for several years for colouring glass.

#### COMPOUNDS OF URANIUM WITH CHLORINE.

§ 1023. Two compounds of uranium with chlorine are known:

The *protochloride*  $\text{UCl}$  is obtained by subjecting a mixture of oxide of uranium and charcoal to the action of chlorine. The mixture being introduced into a tube of hard glass, so as to half fill it, and dry chlorine passed through the end containing the mixture, the latter is heated to redness, when the protochloride of uranium appears in the form of red vapours, which condense in the cold part of the tube in very brilliant and nearly black octahedric crystals. The chloride, which is very susceptible of moisture, dissolves readily in water, and produces a deep-green solution.

If the protochloride be heated in a glass tube in a current of hydrogen gas, it loses a portion of its chlorine, and is converted into a slightly volatile, deep brown product, of which the formula is  $\text{U}_2\text{Cl}_3$ . This chloride dissolves readily in water, and yields a purple solution, which soon turns green by disengaging hydrogen gas.

#### *Oxychloride of Uranium, or Chloride of Uranyle.*

§ 1024. By heating protoxide of uranium in a current of chlorine, a yellow, very fusible, and but slightly volatile crystalline compound is formed, which shows the formula  $\text{U}_2\text{O}_2\text{Cl}$ , or  $(2\text{UO})\text{Cl}$ , if it be regarded as *protochloride of uranyle*. When heated with potassium it loses only its chlorine, and the residue consists of the protoxide ( $2\text{UO}$ ), or uranyle. This compound is soluble in water, with a yellow colour, and forms crystallizable compounds with chloride of potassium and chlorohydrate of ammonia. The formulæ of these double chlorides are  $(2\text{UO})\text{Cl} + \text{KCl} + 2\text{HO}$  and  $(2\text{UO})\text{Cl} + \text{NH}_3, \text{HCl} + 2\text{HO}$ .

#### DETERMINATION OF URANIUM; AND ITS SEPARATION FROM THE METALS PREVIOUSLY STUDIED.

§ 1025. Uranium is determined as protoxide, for which purpose the superior oxides are reduced by hydrogen at a red-heat. It is sometimes weighed in the state of the black oxide  $2\text{UO}, \text{U}_2\text{O}_3$ , in which case it is sufficient to roast the oxides in the air and calcine at a strong red-heat. Sesquioxide of uranium is generally precipitated by ammonia, which yields a yellow precipitate of uranate of ammonia; and as the precipitate is apt to pass through a filter, this inconvenience is remedied by adding a certain quantity of sal-ammoniac to the liquid.

Sesquioxide of uranium is separated from the alkalis by ammonia, and from baryta by sulphuric acid, which precipitates the latter base; while it is separated from lime and strontian by evapo-

rating the liquid with sulphuric acid, and treating it with alcohol, which dissolves only the sesquisulphate of uranium. In order to separate iron from uranium, the former is brought to the state of sesquisalt, and a large excess of carbonate of ammonia is added, which, precipitating the sesquioxide of iron, maintains the uranium in solution. The sesquioxide of uranium may be separated from alumina, and the oxide of chrome by the same process.

The separation of uranium from magnesia and the oxides of manganese, zinc, cobalt, and nickel is founded on the solubility of sesquioxide of uranium in bicarbonate of potassa: an excess of bicarbonate of potassa is poured into the acid liquid, when a soluble double carbonate of sesquioxide of uranium and potassa is formed, while the carbonates of the other metals are precipitated.

In order to separate uranium from cadmium, tin, lead, bismuth, and antimony, it suffices to pass a current of sulphydric acid gas through the acid solution, by which means all these metals are precipitated, while the uranium alone remains in the liquid.

## TUNGSTEN.

EQUIVALENT = 95 (1187.5; O = 100).

§ 1026. Tungsten\* is obtained by heating at a strong red-heat tungstic acid in a current of hydrogen gas in a porcelain tube, when the metal remains in the form of a deep gray powder. It is obtained in a more aggregated form by heating tungstic acid in a "brasqued" crucible in a forge-fire, in which case the metal is in a consistent, but not fused mass, which, when filed, assumes a metallic lustre. Its density is considerable, being about 17.5. It does not oxidize in the air at the ordinary temperature, but at a red-heat is converted into tungstic acid, into which it is also converted when brought at a red-heat into contact with water, which it decomposes. Chlorohydric acid does not act sensibly on metallic tungsten, while nitric acid attacks it actively, and transforms it into tungstic acid, which effect is also produced by sulphuric acid, when concentrated and hot.

## COMPOUNDS OF TUNGSTEN WITH OXYGEN.

§ 1027. Tungsten forms two well-defined compounds with oxygen: a binoxide  $\text{WO}_2$  and tungstic acid  $\text{WO}_3$ .

Tungstic acid, which is the most important of these compounds, is used in the preparation of the other compounds of tungsten. Tungsten occurs in nature as tungstic iron, or *wolfram*,† which is a double tungstate of iron and manganese, of the general formula  $(\text{FeO}, \text{MnO})\text{WO}_3$ ; the formulæ of the minerals from the various localities which have hitherto been analyzed being  $2(\text{FeO}, \text{WO}_3) + 3(\text{MnO}, \text{WO}_3)$ , or  $4(\text{FeO}, \text{WO}_3) + \text{MnO}, \text{WO}_3$ . Wolfram, which is found in large blackish-brown crystals in the primitive rocks, in which it frequently accompanies oxide of tin, is found in many places, particularly in the environs of Limoges. In order to obtain tungstic acid from wolfram, the mineral is treated with aqua regia, which dissolves the iron and manganese as chlorides, while the tungsten remains in the state of insoluble tungstic acid. It is collected on a filter, and, after being well-washed, is treated by a solution of ammonia; when tungstate of ammonia is formed, which dissolves and separates from the quartzose gangue and the untouched ore. The solution yields small prismatic crystals of tungstate of

\* Scheele discovered tungstic acid, while the brothers Elhujart first separated the metal from it.

† In German, the metal is called *wolfram*, after the mineral; or *scheel*, after its discoverer; and from the name of wolfram, the symbol of tungsten, W, is derived. — W. L. F.

ammonia, which, when heated in the air, is converted into tungstic acid.

Tungstic acid is a bright-yellow powder, insoluble in water and the acids, but readily soluble in alkaline liquids and ammonia when it has not been calcined.

By heating tungstic acid at a moderate temperature in a current of hydrogen gas, a brown powder of the *binoxide*  $\text{WO}_2$  remains, the best method of preparing which consists in fusing 1 part of wolfram and 2 of carbonate of potassa in a platinum crucible, and treating the mass with water; after which the filtered liquid containing tungstate of potassa in solution is evaporated to dryness with a  $\frac{1}{2}$  part of sal-ammoniac. The calcined matter being treated with water, the oxide of tungsten  $\text{WO}_2$  remains in the form of a black powder, which changes readily into tungstic acid by heating it in the air. When heated with a concentrated solution of caustic potassa, it decomposes water and is converted into tungstic acid.

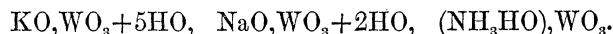
Binoxide of tungsten forms with soda a compound of the formula  $\text{NaO}, 2\text{WO}_2$ , which is obtained by heating bi-tungstate of soda in a current of hydrogen gas, and purified by treatment, first with chlorohydric acid, and then with a solution of potassa, which removes the tungstic acid in excess. The substance forms small cubic crystals of a beautiful golden yellow colour.

When tungstic acid is subjected to a partial reduction, a *blue oxide* is obtained, which is regarded as a compound of the two preceding oxides, having the formula  $\text{WO}_2, \text{WO}_3$ . For this purpose, tungstate of ammonia is decomposed in a close tube, or a blade of zinc is plunged into a liquor containing both tungstic and chlorohydric acids.

#### TUNGSTATES.

§ 1028. No salts formed by a combination of the oxides of tungsten with acids are known, while tungstic acid has been obtained combined with powerful bases. The tungstates of potassa, soda, and ammonia are soluble, while those of the other bases are insoluble. These salts are easily recognised by the residue of tungstic acid which they leave on being decomposed by acids; but in order to obtain a perfect decomposition it is often necessary to boil the tungstate with concentrated acid. Sulphurous acid does not decompose the salts of tungsten, and they are not precipitated by sulphhydric acid and the alkaline sulphhydrates.

The formulæ of the tungstates of potassa, soda, and ammonia, obtained by dissolving tungstic acid, prepared in the humid way, in alkaline solutions, are



Tungstic acid appears to be able to exist under several modifications, corresponding to different degrees of saturation.

## COMPOUNDS OF TUNGSTEN WITH SULPHUR.

§ 1029. Non-calced tungstic acid dissolves readily in the sulphhydrates of the alkaline sulphides, forming sulphotungstates of an alkaline sulphide. By adding an acid to these solutions, *sulphotungstic acid*  $WS_3$  is thrown down in a brown precipitate.

Sulphotungstic acid is decomposed by heat, leaving as a residue *bisulphide of tungsten*  $WS_3$ , in the form of a black powder, which may also be obtained by distilling 1 part of tungstic acid with 5 or 6 times its weight of sulphide of mercury.

## COMPOUNDS OF TUNGSTEN WITH CHLORINE.

§ 1030. Metallic tungsten unites directly with chlorine, with disengagement of light; and if the experiment be made in a heated glass tube, traversed by a current of chlorine, the cold portions of the tube become covered with small deep-red needles of *bichloride of tungsten*  $WCl_2$ , which is very fusible and volatile. Water decomposes it into binoxide of tungsten which is precipitated, and chlorohydric acid.

By heating sulphotungstic acid in a current of chlorine, a trichloride of tungsten  $WCl_3$  is obtained, which sublimes in the form of small red crystals. This chloride is decomposed by water into tungstic and chlorohydric acids.

If gaseous chlorine be passed over tungstic acid, small yellow needles, of the formula  $WO_2Cl_2$ , corresponding in composition to chlorochromic acid (§ 884), sublime in the cooler parts of the tube.

## DETERMINATION OF TUNGSTEN; AND ITS SEPARATION FROM THE METALS PREVIOUSLY STUDIED.

§ 1031. Tungsten is always determined in the state of tungstic acid.

In order to separate it from other metals, either the insolubility of tungstic acid in water and the acids, or its solubility in the alkaline sulphhydrates, is relied on.

The insolubility of tungstic acid in dilute acids insures its separation from the alkaline, alkalino-earthly, and earthy metals, from manganese, iron, chrome, cobalt, nickel, zinc, cadmium, lead, copper, mercury, and silver; while its solubility in ammonia allows its separation from iron, chrome, tin, bismuth, etc. Lastly, its separation from the metals the sulphides of which are not soluble in the sulphhydrates; that is, from iron, zinc, manganese, copper, lead, silver, etc. etc., is effected by its solubility in the alkaline sulphhydrates.

## MOLYBDENUM.

EQUIVALENT = 46 (575.0; O = 100).

§ 1032. Molybdenum\* is obtained by heating in a porcelain tube any oxide of the metal in a current of hydrogen gas; when the molybdenum remains in the form of a gray powder, which, when burnished, assumes a metallic lustre. Molybdenum is obtained in a more aggregated form, by reducing the oxide in a "brasqued" crucible in a forge-fire; and if the temperature be raised as high as possible, small fused masses, having a dead silvery hue, and the density of which is then 8.62, are sometimes obtained. Molybdenum is so easily oxidizable, that that obtained by reduction by hydrogen is entirely converted, when exposed to the air for some time, into a brown powder of the oxide; and by heating the metal in the air it becomes incandescent, and is transformed into molybdic acid. Chlorohydric and dilute sulphuric acid do not attack molybdenum, while nitric acid, on the contrary, acts very powerfully upon it, converting it into molybdic acid.

## COMPOUNDS OF MOLYBDENUM WITH OXYGEN.

§ 1033. Molybdenum forms three compounds with oxygen: the protoxide  $\text{MoO}$  and the binoxide  $\text{MoO}_2$ , which are both bases forming salts; and a third oxide  $\text{MoO}_3$ , which is an acid.

*Molybdic acid*  $\text{MoO}_3$ , which is the most important compound of molybdenum, serves for the preparation of the other combinations of this metal. Molybdenum is chiefly found in nature in the state of sulphide  $\text{MoS}_2$ , forming gray spangles of a metallic lustre, and resembling native graphite, like which substance it leaves gray marks on paper. It occurs in the granitic rocks, frequently accompanying ores of tin, and is principally found in Bohemia and Sweden. After treating the sulphide of molybdenum with aqua regia, which converts the sulphur into sulphuric acid, and the molybdenum into molybdic acid, the liquid is evaporated to dryness and the residue treated with ammonia, which dissolves the molybdic acid during the evaporation of the liquid. The molybdate of ammonia, which separates in crystals, is converted into molybdic acid when heated in the air. Molybdic acid may also be separated by pouring chlorohydric acid into a solution of a molybdate.

Molybdic acid is a white powder, which sublimes at a strong red-heat in white crystalline spangles; which operation can be well

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\* Discovered by Scheele, in 1778.

performed only in a current of gas. Although molybdic acid is very feebly soluble in water when freshly precipitated by an acid, it readily dissolves after calcination. It is easily soluble in the acids.

*Protoxide of molybdenum*  $\text{MoO}$  is obtained by pouring chlorohydric acid into the solution of an alkaline molybdate, until the molybdic acid, which is at first precipitated, is redissolved, when a blade of zinc is plunged into the liquid, which is turned black, after passing through the shades of blue and brownish-red successively. Ammonia is then carefully added to the liquid containing protochloride of molybdenum and chloride of zinc; and, as the protoxide of molybdenum is precipitated first, the addition of ammonia is arrested as soon as the liquid becomes clouded. The precipitate should be washed rapidly, and protected as much as possible from the air, because it is a great absorbent of oxygen.

*Binoxide of molybdenum*  $\text{MoO}_2$  is prepared by decomposing molybdate of ammonia by heat, protected from the air, or by calcining a mixture of molybdate of soda and sal-ammoniac. This oxide, a reddish-brown crystalline powder, forms a reddish-brown hydrate, which resembles the hydrate of sesquioxide of iron.

By adding ammonia to the blue liquid obtained by partially reducing by zinc a chlorohydric solution of molybdic acid, a blue precipitate is formed, which is a saline oxide resulting from the combination of molybdic acid with binoxide of molybdenum.

#### SALTS FORMED BY THE OXIDES OF MOLYBDENUM.

§ 1034. Both the protoxide and binoxide of molybdenum form salts by combining with acids.

These two classes of salts present the following reactions:—The alkalis and ammonia yield brown precipitates, while the alkaline carbonates afford the same coloured precipitate, which dissolves in a large excess of the carbonate of ammonia. Sulfhydric acid precipitates them completely after some time as a black deposit, the same precipitate being formed with the alkaline sulfhydrates; in an excess of which it is soluble. The salts of the protoxide impart to their solutions a brown colour approaching a black, while those of the sesquioxide produce a deep red colour.

#### *Molybdates.*

§ 1035. Molybdic acid forms two series of salts: neutral molybdates  $\text{RO}, \text{MoO}_3$  and bimolybdates  $\text{RO}, 2\text{MoO}_3$ ; the former of which are obtained by dissolving molybdic acid in an excess of alkali, and the latter by boiling a solution of an alkali or an alkaline carbonate with an excess of molybdic acid. The bimolybdates generally crystallize during the cooling of the liquid.

## COMPOUNDS OF MOLYBDENUM WITH CHLORINE.

§ 1036. Metallic molybdenum combines directly with chlorine, yielding at a high temperature a red vapour, which condenses in the form of crystals closely resembling those of iodine. The formula of the chloride, which dissolves freely in water, is  $\text{MoCl}_2$ .

A *protochloride of molybdenum* is obtained by dissolving the hydrated protoxide in chlorohydric acid.

By passing chlorine over heated binoxide of molybdenum, small and very soluble spangles are sublimed, the formula of which is  $\text{MoO}_2\text{Cl}$ , corresponding to chlorochromic and chlorotungstic acids.

## VANADIUM.

EQUIVALENT = 68.6 (857.5; O = 100).

§ 1037. Vanadium\* is an exceedingly rare metal, found in very small quantities in certain Swedish iron-ores, and also occurring in the state of vanadate of lead. Vanadium is obtained by heating vanadic acid with potassium in a platinum crucible; when active reaction takes place, after which the substance is treated with water to dissolve the potassa, and the metal remains in the form of a black powder. It may also be prepared by decomposing chloride of vanadium by ammoniacal gas at a red-heat, in which case it presents the appearance of a flaky, silvery-white mass.

§ 1038. Vanadium forms three compounds with oxygen: the protoxide  $\text{VO}$ , the binoxide  $\text{VO}_2$ , and vanadic acid  $\text{VO}_3$ .

*Vanadic acid* is readily obtained from the native vanadate of lead, by heating the mineral with nitric acid, when vanadic acid is set free, while nitrate of lead is formed. It is treated with water, which leaves the vanadic acid. The acid is dissolved in ammonia, and the vanadate of ammonia crystallized by the evaporation of the liquid, after which it is converted into vanadic acid by calcination in the air. Vanadic acid is an orange-coloured or brown powder, nearly insoluble in water. It is reduced to a lower degree of oxidation by many reducing substances, such as alcohol, sugar, oxalic and sulphurous acids. It dissolves in cold chlorohydric acid, while, if heat be applied, chlorine is disengaged, and the solution contains chloride of vanadium  $\text{VCl}_3$ . By pouring carbonate of potassa into this solution, *hydrated binoxide of vanadium* is precipitated as a gray flaky substance, which dissolves readily in acids, and produces crystallizable salts, of which the solutions are blue.

\* Vanadium was discovered in 1830, by M. Sefström, a Swedish chemist.



By heating vanadic acid in a current of hydrogen gas, a black powder of *protoxide of vanadium* VO is obtained, no saline compounds of which are known.

If a mixture of vanadic acid and charcoal be heated in a current of chlorine, a volatile chloride  $\text{VCl}_3$  is formed, which condenses as a yellow liquid. It boils at a few degrees above  $212^\circ$ , and exhales copious fumes in the air.

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## COPPER.

EQUIVALENT = 31.7 (396.25; O = 100).

§ 1039. Copper has been known from the earliest times. Although it sometimes occurs in the native state, it exists more frequently in combination with oxygen, sulphur, or arsenic. Some salts of the oxide of copper, chiefly carbonates, are also found.

Some kinds of commercial copper are nearly pure; the Russian containing only a trace of iron. Native copper is often crystallized in the form of small, regular octahedrons, which form it also assumes when precipitated slowly from its solutions by galvanic processes, or on being allowed to cool slowly after fusion in a small quantity in a crucible, the liquid portion having been poured off. Chemically pure copper is obtained by reducing pure oxide of copper heated in a tube by means of hydrogen, the reduction taking place at a temperature below a red-heat, and leaving the metal in the form of a red powder, which assumes a brilliant metallic lustre under the burnisher.

Copper has a characteristic red colour, and becomes transparent when reduced to a very thin pellicle; in which case it displays, by transmitted light, a beautiful green colour. Coppery pellicles suitable for the experiment are obtained by reducing by hydrogen, in a heated glass tube, a small quantity of oxide or chloride of copper: when a very thin layer of metallic copper, which displays a red colour by reflected, and a beautiful green by transmitted light, is deposited in certain parts of the tube.

Copper possesses a sufficient degree of malleability to allow its being hammered into thin sheets or drawn out into very fine wire; and at the same time is considerably tenacious, as it requires a weight of 140 kilog. to break a wire of 2 mm. in diameter. The density of copper varies from 8.78 to 8.96, according to the greater or less degree of aggregation it has received during its manufacture. By rubbing, copper acquires a disagreeable smell and a peculiar taste. It fuses at a strong red-heat, and at a white-heat gives off vapours which burn with a green flame in the air.

At the ordinary temperature copper does not oxidize in dry air, but soon changes in a moist atmosphere, especially if acid vapours be present, becoming covered with a green substance commonly called *verdigris*. A blade of copper, moistened by an acid, and exposed to the air, combines with the oxygen of the air, and first produces a neutral salt, which after some time is converted into a basic salt. A blade of copper also oxidizes in the air when moistened with an ammoniacal solution; and dilute solutions of sea-salt attack copper very powerfully, while concentrated solutions exert less influence on it. Copper decomposes aqueous vapour at a strong white-heat, while hydrogen gas is disengaged. A concentrated solution of chlorohydric acid attacks finely divided copper with disengagement of hydrogen, while it scarcely affects the metal in a solid form. Copper does not decompose water in the presence of powerful acids: concentrated sulphuric acid dissolves it with disengagement of sulphurous acid; and it dissolves readily in cold nitric acid of any degree of concentration, with disengagement of deutoxide of nitrogen.

## COMPOUNDS OF COPPER WITH OXYGEN.

§ 1040. Copper forms four compounds with oxygen:

1. The suboxide  $\text{Cu}_2\text{O}$ ,\* or red oxide.
2. The protoxide  $\text{CuO}$ , or black oxide.
3. The binoxide  $\text{CuO}_2$ .
4. Cupric acid, the composition of which is not yet known.

The first two compounds are basic, and form well-defined and crystallizable salts, while the third is an indifferent oxide; and lastly, the fourth is an acid.

*Suboxide of Copper*  $\text{Cu}_2\text{O}$ .

§ 1041. Suboxide of copper is found in nature in masses of a beautiful red colour, possessing occasionally a vitreous lustre, and sometimes consisting of beautiful red crystals. It may be obtained artificially by several processes:—1st, by heating in an earthen crucible equivalent parts of black oxide of copper  $\text{CuO}$  and finely powdered metallic copper; which mixture aggregates when fused at a high temperature; 2d, by heating in a crucible a mixture of chloride of copper  $\text{Cu}_2\text{Cl}$  with carbonate of soda, and then treating the substance with water, which dissolves the chloride of sodium and excess of carbonate of soda, leaving the suboxide of copper in the form of a deep red crystalline powder; 3d, by adding to a solution of a salt of copper, for example, the sulphate  $\text{CuO}, \text{SO}_3$ , sugar and potassa, until the oxide of copper, which is at first precipitated, is

\* The name of *protoxide of copper* is often given to the suboxide  $\text{Cu}_2\text{O}$ , and that of *binoxide of copper* to the oxide  $\text{CuO}$ . We shall not adopt this nomenclature because it does not agree with that which we have thus far adopted.

redissolved, and by then boiling the liquid; when suboxide of copper is deposited in the form of small bright-red crystals.

Hydrated suboxide of copper is obtained by adding potassa to a solution of protochloride of copper, in the form of a yellow powder, which soon absorbs oxygen from the air, and which, when dried in vacuo, presents the formula  $4\text{Cu}_2\text{O} + \text{HO}$ . Hydrated suboxide of copper dissolves in ammonia without colouring the liquid, but by its rapid absorption of oxygen from the air soon changes the colour of the solution to a beautiful blue.

Suboxide of copper imparts a beautiful red colour to fluxes (§ 702). When heated with concentrated acids it is generally decomposed into protoxide of copper  $\text{CuO}$  which dissolves, and metallic copper which is separated.

#### *Protoxide of Copper* $\text{CuO}$ .

§ 1042. On heating metallic copper in the air, its surface first becomes covered with suboxide  $\text{Cu}_2\text{O}$ , which subsequently changes into the black oxide  $\text{CuO}$ . Although protoxide of copper is often prepared by roasting copper turnings, or better still, the very finely divided copper which remains after the calcination of the acetate with access of air, it is obtained more readily by decomposing the nitrate by heat, when the oxide remains in the form of a black powder, which rapidly condenses the moisture of the atmosphere.

When caustic potassa is poured into the solution of a protosalt of copper, a grayish-blue precipitate of hydrated protoxide is formed, the water of which is readily driven off by heat: it suffices to boil the solution in which it has been precipitated to convert it into a black powder of anhydrous oxide. Hydrated protoxide of copper dissolves in ammonia, producing a solution of a slightly purple-blue colour, called *celestial water*.

#### *Deutoxide of Copper.*

§ 1043. This oxide is prepared by treating the hydrated protoxide of copper with oxygenated water, when the blue matter is changed into a brownish-yellow substance, from which a slight elevation of temperature easily abstracts one-half of its oxygen.

#### *Cupric Acid.*

§ 1044. An intimate mixture of very finely divided copper, potassa, and nitre, heated to redness and then treated with water, yields a blue solution which appears to contain a combination of an oxide of copper containing more oxygen than the preceding with potassa. This compound, however, is so evanescent that, if the liquid be heated, oxygen is disengaged, and the copper is precipitated in the state of black oxide  $\text{CuO}$ .

SALTS FORMED BY THE SUBOXIDE OF COPPER  $\text{Cu}_2\text{O}$ .

§ 1045. The salts of the suboxide of copper are obtained by dissolving hydrated suboxide in dilute acids, which, when they are concentrated, decompose the suboxide into metallic copper which separates, and protoxide which combines with the acids.

A *subsulphite of copper*  $\text{Cu}_2\text{O}, \text{SO}_2$ , is prepared by decomposing a solution of protosulphate of copper  $\text{CuO}, \text{SO}_3$  by a solution of sulphite of soda, when an orange precipitate is formed which is converted, by boiling, into a red crystalline powder.

When acetate of copper is distilled, a small quantity of a white sublimate, consisting of *sub-acetate of copper*, is found in the upper part of the retort.

The soluble subsalts of copper produce colourless solutions, from which alkalies throw down an orange-yellow precipitate. Ammonia gives the same reaction, but an excess of the reagent redissolves the precipitate, producing a colourless liquid which soon turns blue in the air. Sulfhydryc acid throws down a black precipitate of these salts, for the study of whose reactions the subchloride  $\text{CuCl}$  is exactly suitable.

SALTS FORMED BY THE PROTOXIDE OF COPPER  $\text{CuO}$ .

§ 1046. These salts, which are obtained by dissolving protoxide of copper, or better still, its hydrate or its carbonate, in acids, are blue or green, when they contain water of crystallization, while in the anhydrous state they are of a dirty white, when the acid is colourless, and their solutions are blue or green. They exhibit the following characteristic reactions:

Caustic potassa and soda yield a grayish-blue precipitate of hydrated protoxide, which is converted into a brown precipitate by boiling. The blue precipitate, which is insoluble in weak alkaline liquids, dissolves with a blue colour in the latter when they are concentrated.

Ammonia throws down the same precipitate, while an excess of the reagent dissolves the precipitate and produces a beautiful blue solution, which then contains a double salt of copper and ammonia, from which caustic potassa precipitates oxide of copper.

Sulfhydryc acid and the sulfhydrates throw down black precipitates, which are insoluble in an excess of sulfhydrate.

Prussiate of potash forms, with protosalts of copper, a chestnut-brown precipitate, which assumes a purplish shade when the precipitate is very weak. The test is a very delicate one, and will detect the presence of the smallest quantities of copper in a solution.

Iron and zinc precipitate metallic copper in the form of a brown powder, which, when burnished, assumes the metallic lustre and ordinary appearance of copper.

Protoxide of copper turns borax, and in general all vitreous

fluxes, green. If the glass be heated in the reducing portion of the flame, it acquires a beautiful red colour, produced by the reduction of the protoxide of copper  $\text{CuO}$  into the suboxide  $\text{Cu}_2\text{O}$ .

*Sulphate of Copper.*

§ 1047. Sulphate of copper is found in commerce, where it is known by the name of *blue vitriol*, in which state it generally contains variable quantities of sulphate of iron. It may be obtained in a state of purity by treating copper of the first quality with sulphuric acid diluted with one-half its weight of water; when sulphurous acid is disengaged, and sulphate of copper is formed which contains only a trace of sulphate of iron. It is evaporated to dryness, and, toward the close of the evaporation, a few drops of nitric acid are added, which convert the iron into sesquioxide. By dissolving it in water the greater portion of the iron remains in the state of an anhydrous basic sesquisulphate; when, after boiling the liquid with a small quantity of the hydrate or carbonate of the protoxide of copper, which precipitates the least traces of iron, the liquor is crystallized.

Sulphate of copper is soluble in 4 parts of cold and 2 parts of boiling water, and crystallizes at the ordinary temperature in beautiful blue crystals, which belong to the sixth system, and of which the formula is  $\text{CuO}, \text{SO}_3 + 5\text{H}_2\text{O}$ . They are isomorphous with those produced by protosulphate of iron when crystallized at a temperature of about  $40^\circ$ , and which likewise contain 5 equiv. of water. When these two sulphates are mixed together, and the compound solution is crystallized, crystals are deposited containing the two sulphates in different proportions, according to the respective quantities of the salts in the solution. A crystal of sulphate of copper may even be made to grow at pleasure, in a solution of sulphate of iron. The crystal then increases by the superaddition of layers of sulphate of iron, which are easily distinguished by their colour. The same crystal, suspended in a solution of sulphate of copper, becomes covered with layers of this latter sulphate, without any remarkable change in its external appearance.

Sulphate of copper readily parts by heat with 4 equiv. of water, but retains the fifth with more tenacity. It is entirely decomposed at a high temperature, into oxide of copper which remains, and a mixture of sulphurous acid and oxygen which is disengaged.

Sulphate of copper is manufactured in various ways; and a certain quantity of this salt is obtained in copper furnaces. When sulphuretted copper ores or cupreous matts, are roasted, and the roasted matter is sprinkled with water, a certain quantity of the sulphates of iron and copper is dissolved, and separates by crystallization. The sulphate of copper thus obtained, always contains a large proportion of sulphate of iron.

Large quantities of sulphate of copper are manufactured from the

copper sheathing of ships which has been rendered useless by the corrosive action of salt water. The copper is heated to a dull red-heat in a reverberatory furnace, and sulphur thrown in, the doors of the furnace being previously closed, when the sulphur attacks the surface of the copper, covering it with sulphide of copper  $\text{Cu}_2\text{S}$ , after which it is roasted, and air allowed to enter the furnace freely. A portion of the sulphur is then disengaged in the state of sulphurous acid, while another portion changes into sulphuric acid, and forms a basic protosulphate of copper. The sulphatized sheets are then placed in large boilers filled with water, to which a certain quantity of sulphuric acid has been added, when neutral protosulphate of copper dissolves, and is crystallized by evaporation as soon as the liquid contains a sufficient quantity of it. This process is repeated until the sheets of copper have disappeared.

Large quantities of sulphate of copper have been obtained in the refining of old silver coin, as we shall mention hereafter.

If sulphate of copper be dissolved in a hot solution of ammonia, a beautiful blue solution is obtained, which deposits on cooling deep blue crystals, the composition of which is represented by the formula  $\text{CuO}, \text{SO}_3 + 2\text{NH}_3 + \text{HO}$ .

By digesting hydrated oxide of copper with a solution of protosulphate of copper, a green powder, consisting of a hydrated basic sulphate of copper  $\text{CuO}, \text{SO}_3 + 2\text{CuO} + 3\text{HO}$  is obtained. Analogous basic sulphates are precipitated when solutions of sulphate of copper are incompletely precipitated by the alkalies.

Sulphate of copper forms with the alkaline sulphates double salts which are readily crystallizable, and also produces double sulphates, of various proportions, with the sulphate of magnesia, and with those of the protoxides of iron, zinc, nickel, etc., which are all isomorphous. These double sulphates, crystallized at the ordinary temperature, contain 5 equiv. of water when the sulphate of copper predominates, and 7 equiv. of water, on the contrary, when the other metallic sulphate is prevailing. In both cases, the sulphates are isomorphous whenever they contain the same quantity of water.

#### *Nitrate of Copper.*

§ 1048. This salt is prepared by dissolving copper in dilute nitric acid, when the liquid yields on evaporation beautiful blue crystals, which contain 3 or 6 equiv. of water, according to the temperature at which the crystallization has been effected. It is used in dyeing.

The influence of heat changes nitrate of copper into the green basic nitrate  $4\text{CuO}, \text{NO}_3$ , and subsequently decomposes it at a more elevated temperature, leaving protoxide of copper. The same basic nitrate is obtained by precipitating the neutral nitrate of ammonia.

#### *Carbonates of Copper.*

§ 1049. By adding a solution of an alkaline carbonate to a solu-

tion of sulphate of copper, a bright blue gelatinous precipitate is obtained, which, after some time, changes into a green powder, the composition of which is represented by the formula  $2\text{CuO}, \text{CO}_2 + \text{HO}$ ; the blue gelatinous precipitate appearing to differ from it only in containing more water. By boiling the liquid with the precipitate, the latter is converted into a brown powder of anhydrous protoxide of copper. The green carbonate of copper is used in oil-painting, under the name of *mineral green*.

A hydrocarbonate of copper, of the formula  $\text{CuO}, \text{CO}_2 + \text{CuO}, \text{HO}$ , called *malachite*, is found in nature in the form of green concrete masses, which are often very compact and of considerable size, and are fashioned into ornamental objects, such as vases, shafts of columns, and table and chimney tops, which are of great value. When polished they display veins of different shades of colours, which are produced by the mammillary structure of the material, and impart a very beautiful appearance to the polished surfaces. Malachite is sufficiently abundant in Siberia to be worked as an ore of copper.

Another hydrocarbonate of copper, of which the formula is  $2\text{CuO}, \text{CO}_2 + \text{CuO}, \text{HO}$ , and which yields fine blue crystals, also occurs in nature, which substance existed in great abundance in the mines of Chessy, near Lyons, where it was long smelted as an ore of copper. When finely powdered it is of a beautiful blue colour, in which state it is used in the manufacture of coloured wall-paper, and is called *mountain blue*, or *native blue ashes*, (*bleu de montagne*, or *cendres bleues naturelles*.) *Artificial blue ashes*, of a more brilliant shade than the native product, are made in England, by a process which is kept secret.

#### *Arsenite of Copper.*

§ 1050. Arsenite of copper, which is used in oil-painting, under the name of *Scheele's green*, is prepared by dissolving 3 kilog. of carbonate of potassa, and 1 kilog. of arsenious acid in 14 litres of water, and pouring the solution, by small quantities at a time, into a boiling solution of 3 kilog. of sulphate of copper in 40 litres of water, the solutions being stirred constantly during the precipitation. The shade of colour is modified by varying the proportions of arsenious acid.

#### *Silicates of Copper.*

§ 1051. By means of fusion the oxide of copper combines in all proportions with silicic acid, forming green vitreous substances. A crystallized silicate of copper, called *diopase* by mineralogists, is found in nature, and presents the formula  $3\text{CuO}, 2\text{SiO}_2 + 3\text{HO}$ .

#### *Acetates of Copper.*

§ 1052. By dissolving protoxide of copper in acetic acid, a green liquid is obtained, which, when evaporated at a proper temperature,

deposits beautiful green crystals of the formula  $\text{CuO}, \text{C}_4\text{H}_3\text{O}_3 + \text{HO}$ , and which are soluble in 5 parts of boiling water. It is known in commerce by the name of *verdigris*, and is manufactured by dissolving the basic acetate of copper in vinegar. When the salt crystallizes at a low temperature, the crystals are blue, and present the formula  $\text{CuO}, \text{C}_4\text{H}_3\text{O}_3 + 5\text{HO}$ .

A basic acetate of copper is prepared in the South of France by allowing sheets of copper, moistened with vinegar or brought into contact with the grape mash which is undergoing the acid fermentation, to oxidize in the air. The copper sheets become covered with a greenish-blue coat, which is scraped off from time to time, and of which the formula is  $\text{CuO}, \text{C}_4\text{H}_3\text{O}_3 + \text{CuO}, \text{HO} + 5\text{HO}$ . If it be treated with water, insoluble crystalline spangles of the formula  $3\text{CuO}, \text{C}_4\text{H}_3\text{O}_3$  separate, while a mixture of neutral acetate  $\text{CuO}, \text{C}_4\text{H}_3\text{O}_3$  and basic acetate  $3\text{CuO}, 2\text{C}_4\text{H}_3\text{O}_3$  dissolves.

A basic acetate of copper is made at Grenoble, by exposing sheets of copper moistened with vinegar in hot stoves. This substance appears to be a mixture of the two sub-acetates  $3\text{CuO}, 2\text{C}_4\text{H}_3\text{O}_3$  and  $3\text{CuO}, \text{C}_4\text{H}_3\text{O}_3$ .

A colour which is a compound of acetate and arsenite of copper  $\text{CuO}, \text{C}_4\text{H}_3\text{O}_3 + 3(2\text{CuO}, \text{AsO}_3)$  is likewise used in oil-painting, under the name of *Schweinfurt green*, and is prepared by mixing boiling solutions of equal parts of arsenious acid and acetate of copper, and boiling the mixture for some time.

#### COMPOUNDS OF COPPER WITH SULPHUR.

§ 1053. Copper burns actively in the vapour of sulphur (§ 306), while a sulphide of copper  $\text{Cu}_2\text{S}$  corresponding to the suboxide  $\text{Cu}_2\text{O}$  is formed. This sulphide fuses more easily than metallic copper, and becomes crystalline on cooling: it is sometimes found in copper furnaces, crystallized in regular octahedrons. It is prepared in the laboratory by heating a mixture of 3 parts of sulphur and 8 of copper turnings, grinding the substance obtained again to powder, and reheating with sulphur. This sulphide of copper exists in nature, and sometimes forms beautiful crystals, which are sufficiently soft to be cut with a knife.

The sulphide of copper  $\text{CuS}$  corresponding to the protoxide  $\text{CuO}$  cannot be prepared by the humid way, by decomposing the solution of a protosalt of copper by sulphhydric acid or a sulphhydrate, as the black powder thus obtained soon changes in the air. In analyses, it is necessary to wash it with water containing a small quantity of sulphhydric acid. The sulphide of copper  $\text{CuS}$ , when heated, parts readily with one-half of its sulphur, and is converted into the sulphide  $\text{Cu}_2\text{S}$ .

Compounds of sulphide of copper  $\text{Cu}_2\text{S}$  and sulphide of iron  $\text{Fe}_2\text{S}_2$  in very various proportions are found in nature, constituting minerals which are called *copper pyrites*, *pyritous copper*, and *variegated*



*copper*, according to their external mineralogical characters, which frequently agree with their chemical composition. These minerals are very important, as they are the most common ores of copper, and furnish the largest proportion of this metal.

#### COMPOUND OF COPPER WITH ARSENIC.

§ 1054. Copper, heated in a vapour of arsenic, combines readily with a small quantity of this substance, becoming white and very brittle; but hitherto no definite compound of these substances has been obtained.

#### COMPOUND OF COPPER WITH PHOSPHORUS.

§ 1055. A gray and very brittle phosphuret of copper, containing about 20 per cent. of phosphorus, is formed when very finely divided copper is heated in the vapour of phosphorus. A definite compound of copper and phosphorus  $\text{Cu}_2\text{P}$  is obtained by decomposing neutral phosphate of copper by hydrogen at a low temperature. Phosphurets of copper are also obtained by the humid way, by passing a current of phosphuretted hydrogen gas through a solution of sulphate of copper.

#### COMPOUND OF COPPER WITH NITROGEN.

§ 1056. A nitride of copper of the formula  $\text{Cu}_3\text{N}$  is obtained by heating, at a temperature of  $509^\circ$ , oxide of copper  $\text{CuO}$  in a current of dry ammoniacal gas, when the substance is treated with a solution of ammonia, which dissolves the oxide of copper in excess. Nitride of copper is a deep green powder, which is easily decomposed by heat, with a slight explosion.

#### COMPOUND OF COPPER WITH HYDROGEN.

§ 1057. A compound of copper with hydrogen is obtained by heating, at a temperature of  $158^\circ$ , a solution of sulphate of copper with hypophosphorous acid. The hydride of copper thus prepared is hydrated, and forms a bright brown powder, which suddenly decomposes at about  $140^\circ$  into metallic copper and hydrogen gas, which is disengaged. Chlorohydric acid decomposes it, forming protochloride of copper, while the hydrogen is set free.

#### COMPOUNDS OF COPPER WITH CHLORINE.

§ 1058. Two compounds of copper with chlorine are known: the first  $\text{Cu}_2\text{Cl}$  corresponds to the suboxide, while the second  $\text{CuCl}$  corresponds to the protoxide.

*Subchloride of copper*  $\text{Cu}_2\text{Cl}$  is obtained by boiling a solution of protochloride of copper  $\text{CuCl}$  with very finely divided metallic copper, when the colour of the liquid changes from green to brown, while white crystalline chloride of copper  $\text{Cu}_2\text{Cl}$  is soon deposited.

The chloride is also obtained by decomposing the protochloride  $\text{CuCl}$  by heat, the latter parting with one-half of its chlorine. The protochloride  $\text{CuCl}$  may be reduced to the state of subchloride  $\text{Cu}_2\text{Cl}$  by pouring protochloride of tin into a solution of protochloride of copper, the decomposition taking place in the cold, while chlorohydric acid, which prevents the precipitation of the oxide of tin, is added to the liquid. The chloride  $\text{Cu}_2\text{Cl}$  may be obtained crystallized in small tetrahedrons by dissolving it, assisted by heat, in chlorohydric acid, when the chloride is deposited during the cooling of the liquid.

Chloride of copper  $\text{Cu}_2\text{Cl}$  fuses at a temperature of about  $752^\circ$ , and volatilizes at a red-heat. It is very slightly soluble in water, but dissolves more freely in chlorohydric acid, and particularly in ammonia. It soon alters in the air, and is converted into a green powder consisting of a compound of hydrated oxide of copper  $\text{CuO}$  and protochloride  $\text{CuCl}$ . In consequence of the affinity of this substance for oxygen, it is frequently used in eudiometric analyses, and generally in the form of solution in ammonia.

*Subchloride of copper*  $\text{CuCl}$  is obtained by dissolving the protoxide  $\text{CuO}$  in chlorohydric acid, or by dissolving metallic copper in aqua regia. The chloride is very soluble in water, and crystallizes on cooling from a concentrated solution in the form of long bluish-green needles, of which the formula is  $\text{CuCl} + 2\text{HO}$ .

This chloride is prepared in the anhydrous state by slightly heating copper in an excess of chlorine, when a yellowish-brown compound is obtained, which evolves chlorine when heated to a dark red-heat, and is converted into the chloride  $\text{Cu}_2\text{Cl}$ . The chloride dissolves readily in alcohol, and imparts to it the quality of burning with a beautiful green flame.

#### DETERMINATION OF COPPER, AND ITS SEPARATION FROM THE METALS PREVIOUSLY DESCRIBED.

§ 1059. Copper is determined either as anhydrous protoxide  $\text{CuO}$  or in the metallic state. When copper exists alone in a liquid, it is precipitated by caustic potassa, after which the liquid should be boiled, because the hydrated protoxide is then changed into an anhydrous oxide, which is more easily washed: the oxide is weighed after being calcined in the air. Copper is frequently precipitated by a blade of iron or zinc, and, if it is to be weighed in this state, must be rapidly washed with boiling water and dried excluded from the air, from which it promptly absorbs oxygen. When copper is precipitated from its solutions by sulfhydric acid gas, the precipitate must be washed with water charged with sulfhydric acid, while the filter on which the substance has been collected must be calcined, and the whole dissolved in aqua regia, from which solution the copper is then precipitated by caustic potassa.

Copper is very accurately determined by the following process, used in the analysis of many cupreous substances :

The substance being dissolved in an acid, an excess of ammonia is added to it, which redissolves the oxide of copper, forming a blue solution, remarkable for its great colouring power. A standard solution of sulphide of sodium is poured into the liquid from an alkalimeter ; when the copper is precipitated in the state of an oxysulphide of the formula  $\text{CuO}, 5\text{CuS}$ . By careful manipulation, the moment at which the copper is entirely precipitated may be exactly ascertained, as the reaction is finished when the liquid has lost its colour. It is then easy to calculate the quantity of copper precipitated, from the volume of the standard solution of sulphide of sodium, supposing always that no other substances which are precipitable by the alkaline sulphide exist in the liquid.

In order to prepare the standard solution of sulphide of sodium, 1 gm. of pure copper is dissolved in 5 or 6 gm. of nitric acid ; and about 50 gm. of a concentrated solution of ammonia being added, gentle heat is applied to dissolve completely the precipitate. The solution of sulphide of sodium, the initial volume of which has been measured on the division of the alkalimeter containing it, is then poured into the deep-blue liquid ; and when the latter is only of a light blue, the flask is shaken several times, and then allowed to rest for a few moments. The sulphide of sodium is then added, drop by drop, in order to observe exactly the moment at which the liquid loses its colour, at which point the volume of solution added is marked on the division of the alkalimeter. Supposing this volume to be represented by 137.5 div., it will be thence inferred that 137.5 div. of the solution of sulphide of sodium correspond to 1.000 gm. of metallic copper ; and consequently, if, in order to remove the colour of an ammoniacal cupreous liquid, 97.5 div. of the solution of sulphide of sodium are required, the conclusion follows that the tested solution contained  $\frac{97.5}{137.5} \cdot 1.000$  gm., or 0.709 gm. of metallic copper.

The described process may be applied to solutions containing other metals than copper, as experiment has shown that it gave exact results even when the liquid contained iron, zinc, cadmium, tin, and lead or antimony, because the alkaline sulphide only commences to act on the metals named after the copper has been completely precipitated in the state of oxysulphide. It is nevertheless indispensable that the iron should be in the state of sesquioxide, since the presence of protoxide would derange the result. It is not necessary to separate by filtering the deposit thrown down by several of these metals at the moment of adding the excess of ammonia ; although it may be of advantage when the deposit is very copious, because the latter would prevent the colour of the liquid from being distinguished.

The process of determination just described becomes inaccurate

when the liquor contains cobalt, nickel, mercury, or silver. The presence of silver may be easily avoided, as it is sufficient to add a few drops of sulphydric acid to the nitric solution, when the silver is entirely precipitated as insoluble chloride.

§ 1060. Copper is easily separated from the alkaline, alkalino-earthly, and earthy metals, from manganese, iron, chrome, cobalt, nickel, zinc, titanium, and uranium, by means of sulphydric acid, passed through the liquid acidulated by chlorohydric acid, when the copper alone is precipitated in the state of sulphide.

It is separated from cadmium, bismuth, and lead, when these metals are dissolved in nitric acid, by means of an excess of carbonate of ammonia, which does not dissolve the copper; which same process may be employed to separate copper from alumina and the sesquioxides of iron and chrome; but the results are less exact than those of precipitation by sulphydric acid. The best method of separating copper from lead is to add sulphuric acid to the nitric solution of the two metals, and evaporate to dryness to drive off the excess of acid, when the residue, after being moistened with a small quantity of nitric acid and treated with water, consists only of sulphide of lead.

Copper is separated from tin by treating the two metals with nitric acid, evaporating to dryness, moistening the residue with a small quantity of nitric acid, and dissolving it in water, when the tin remains in the state of stannic acid. By the same process, copper may be separated from antimony; but the results are less exact, because a small proportion of antimony is always dissolved. It is therefore better, after having dissolved the metals in aqua regia, to saturate the solution by ammonia, and add an excess of sulphhydrate of ammonia, in which sulphide of antimony is soluble. The same process will serve to separate copper from tin and arsenic.

#### METALLURGY OF COPPER.

§ 1061. Copper is found in nature chiefly in the state of sulphide, which is rarely isolated, being generally combined with sulphide of iron, constituting copper pyrites  $\text{Cu}_2\text{S} + \text{Fe}_2\text{S}_3$ , and frequently mixed, in greater or less proportions, with iron pyrites  $\text{FeS}_2$ . The most common ores of copper are therefore mixtures of sulphide of iron and copper. Besides copper pyrites, the following ores occur: *variegated copper*  $2\text{Cu}_2\text{S} + \text{FeS}$ ; *fahlerz*, or *gray copper*, which is a double sulphide of antimony and copper; and *bournonite*, which is a multiple sulphide of antimony, copper, and lead; all of which are very important minerals, being generally very rich in silver. All the ores just named are found in veins traversing the old rocks; while near these primitive veins deposits of copper ores are often seen, evidently arising from the alteration of the ore by the action of water. When slow streams of water, which, in their course, pass over beds of copper ore, and thus generally contain sulphate of copper, drop

into calcareous earths, or remain in the cavities of calcareous rocks, sulphate of lime is formed and carried off by the water, while carbonate of copper is deposited; and if the reaction takes place at a high temperature, oxide of copper is deposited instead of the carbonate. Lastly, if organic substances be present, the sulphate of copper may be reduced either to the metallic state or to that of sulphide of copper. The occurrence of masses of carbonate and oxide of copper, which are frequently found near veins of copper pyrites, is thus explained, as is also the origin of small crystals of sulphide of copper scattered through certain schistose rocks which are impregnated with bitumen and contain many organic remains. In this way, geologists explain the formation of the cupreous pyrites found scattered in small crystals through bituminous schist, and exhibiting impressions of fishes, which form the bottom of a very extensive basin of secondary rocks in Mansfeld, in the north of Germany.

More or less considerable masses of suboxide of copper  $\text{Cu}_2\text{O}$  are sometimes found, which yield a very rich copper ore, very valuable mines of which are in Peru and Chili. The principal localities of copper ore in Europe are in the county of Cornwall in England, Mansfeld and Rammelsberg in the north of Germany, in Sweden, Norway, and the Ural and Altai mountains in Russia. There formerly existed at Chessy and Saint-Bel, near Lyons, a very productive mine of oxide and carbonate of copper, which is now exhausted.\*

§ 1062. The ores of the oxide and carbonate of copper are very easily worked. It is sufficient to smelt them in contact with charcoal, in cupola furnaces, with scorïæ more or less silicious, when an impure copper, called *black copper*, is obtained, which, after refining, yields marketable copper.

§ 1063. The treatment of the sulphuretted ores is much more complicated. They are first subjected to several preliminary roastings, in order to convert a certain portion of the sulphides into oxides, after which the roasted ores are smelted in blast or in reverberatory furnaces, with the addition of scorïæ or other fluxes, if the ore does not itself contain a sufficient proportion of silicates. Copper has a greater affinity for sulphur than iron, while the latter metal, on the contrary, has a greater affinity for oxygen, especially in the presence of silicic acid; the oxide of copper, which forms during the roasting, therefore passes entirely into the state of sulphide, by abstracting the sulphur from the sulphide of iron which remained in the roasted material, the products of the operation being a slag, which contains the greater part of the iron of the

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\* The principal locality of copper ores in the United States is that at Keweenaw Point, Lake Superior, where large masses of native copper are found. Other great localities, omitted in the text, are those in Cuba, Siberia, and Burra Burra in Australia, all of which yield principally oxidized ores.—*W. L. F.*

copper pyrites, and a sulphide of iron and copper, and the *cupreous matt*, containing nearly all the sulphide of copper of the pyrites, and a much smaller proportion of sulphide of iron. The matt is, consequently, a sulphuretted ore of copper, much richer in copper than the original pyrites. It is again roasted, and melted with silicious scoriæ, and frequently with ores of oxide of copper, when they are at hand, which process produces a new slag, containing a great portion of the iron of the first matt, and a second cupreous matt, still richer in copper than the first. These successive operations are repeated until an impure copper, *black copper*, a last cupreous matt, and scoriæ, are obtained, the matt being then subjected to similar processes, or added to the preceding matt, so that the ultimate product is black copper, which is refined. We shall give examples of this metallurgic process as adopted in some of the most important European works.

§ 1064. At Fahlun, in Sweden, the principal ore is copper pyrites, mixed intimately with iron pyrites and accompanied by a quartzose gangue. The pyritous ores are roasted, mixed with silicious ores, in the proportion of 2 parts of pyritous and 1 of silicious ore, and 10 to 30 per cent. of scoriæ, arising from a previous smelting, added. This mixture is smelted in a blast-furnace of about 3 metres in height, and a matt composed of sulphide of iron  $\text{Fe}_2\text{S}$  and sulphide of copper  $\text{Cu}_2\text{S}$ , with a slag which should present nearly the composition of bisilicate of iron  $\text{FeO}, 2\text{SiO}_2$ , are removed from it. The matt, which contains 8 to 10 per cent. of copper, is subjected to four successive roastings, which remove nearly all the sulphur and leave the metals in the state of oxide. The roasted matts are smelted in blast-furnaces, resembling those used for the smelting of the roasted ores, quartz and oxidized or sulphuretted silicious ores which have been previously roasted being added. This smelting yields black copper, a small quantity of cupreous matt, and scoriæ, which are chiefly simple silicates of iron  $\text{FeO}, \text{SiO}_2$ . The cupreous matt is then treated like the first matt arising from the smelting of the ores, while the black copper is refined by a process soon to be described.

§ 1065. The copper ores of Mansfeld are argillaceous schists, containing pyrites scattered through in small crystals, their richness in copper being very variable, while they are strongly impregnated with bitumen. They are roasted by being heaped on a pile of wood, which is easily done, the consumption of fuel being small, as the fire is kept up by the bitumen. Five to eight per cent. of fluor-spar, scoriæ poor in copper, arising from subsequent operations, and frequently small quantities of cupreous schists containing carbonate of lime, are added, and the mixture is smelted in blast-furnaces 5 or 6 metres high, heated by coke. Fig. 558 represents a vertical section of the furnace passing through one of the twyers, while fig. 557 represents a front view. (The breast of the furnace has

been removed to show the interior.) The lower part of the furnace is built of quartzose sandstone, and the upper part of bricks. The

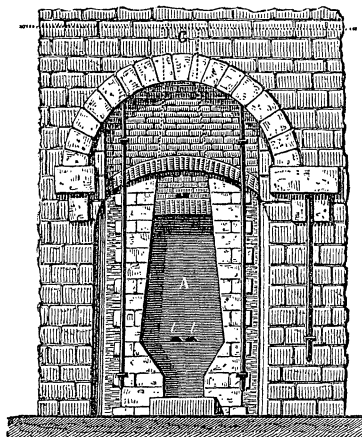


Fig. 557.

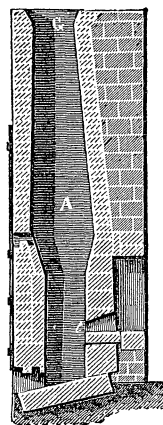


Fig. 558.

furnace has two twyers, either on the same side, as in fig. 559, or on opposite sides. At the base of the breast of the furnace are two openings *o, o'*, which are opened alternately for the escape of the liquid products, and which communicate by means of canals with

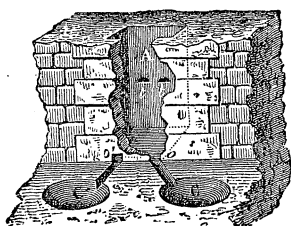


Fig. 559.

two large crucibles *C, C'* outside. The smelter allows a nose of 0.2 m. in length to form in front of the twyers, and the fuel and ore are charged alternately in layers. The furnaces are surmounted by chimneys of 12 or 15 metres in height, to carry off the products of combustion. The matts and scoriæ escape constantly from the furnace, and flow into one of the receiving basins *C*, the opening *o'* corresponding to the basin *C'* being closed. When the crucible *C* is filled, the hole *o'* is opened and the material allowed to run into *C'*, after which the products in the basin *C* are immediately removed. The slags are generally moulded into large bricks, which are used in building; while the matts, in the shape of disks, are removed as fast as their surface solidifies. The crucible *C* being emptied, when *C'* is filled, the substances flowing from the furnace are again collected.

The matt, which forms only about  $\frac{1}{10}$  of the weight of the melted ores, is composed of sulphide of iron  $\text{FeS}$  and sulphide of copper  $\text{Cu}_2\text{S}$ ; its proportion of copper varying from 20 to 60 per cent., according to the nature of the ore. When the matt contains only 20 or 30 per cent. of copper, it is subjected to three successive

roastings on heaps of wood, and is again passed through the furnace, with the addition of a certain quantity of slag arising from the first smelting of the ores; for which purpose the slag which immediately covered the matt in the receiving basins, and which is richer than the superficial scoriæ, is selected. A new matt is thus obtained, presenting the same percentage of copper as that arising from the smelting of rich ores.

§ 1066. The rich matts are subjected to six successive roastings on heaps of wood, the operation being performed in small stalls

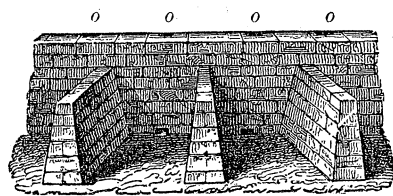


Fig. 560.

(fig. 560), formed by three stone walls, and having openings at *o*, to facilitate the draught. The matt which has been roasted in the first stall is passed to that of No. 2, and so on until it reaches No. 6. A considerable quantity of sulphate of copper, which is formed during the roasting, is subsequently removed by washing, as it can be sold to a good profit. Beginning with the third roasting, the matts are lixiviated, after each roasting, in large wooden boxes, superimposed upon each other, a methodical process of washing (§ 447) being adopted, so that the water which flows from the last box is nearly saturated, and soon deposit crystals when evaporated by heat in leaden boilers.

The roasted matt is smelted in a blast-furnace resembling that in which the ores are smelted, but smaller; the scoriæ intended to combine with the oxide of iron of the matt being added. This smelting yields black copper, scoriæ, and a matt which, being very rich in copper, is added to the second matts resulting from the preceding operation. The black copper is removed in disks, for which purpose a small quantity of water is poured on the melted mass, to render the superficial stratum solid. Black copper contains about 95 per cent. of copper, 3 or 4 of iron, and small quantities of silver and antimony.

§ 1067. Cupreous ores often contain enough silver to render the extraction of this metal advantageous; which operation is effected either on the black copper or on the last roasted matts. The black copper is worked by *eliquation*, and the matts by *amalgamation*. The following is the principle of eliquation:—By fusing copper and lead in an elbow-furnace, the two metals are alloyed; and if the fused alloy be suddenly cooled at the moment of its escape from the furnace, the metals remain intimately mixed. But, if the solid alloy be gradually reheated, or if the melted alloy be slowly cooled, the metals separate, and the lead retains all the silver which originally existed in the copper, while the latter metal is merely com-



bined with a certain quantity of lead. By cupellation the lead gives up its silver, and the impure copper is refined.

Three parts of black copper, and 10 or 12 parts of lead, as argentiferous as possible, are fused in a small elbow-furnace, litharge rich in silver being often substituted for the lead. The fused alloy is run into cast-iron moulds, where it suddenly cools,

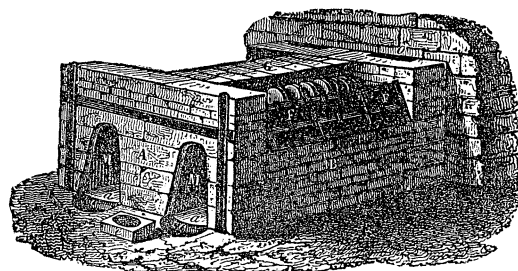


Fig. 561.

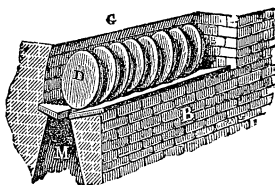


Fig. 562.

and takes the shape of disks, which are heated on the *eliquating furnace*. This apparatus consists of two cast-iron plates (figs. 561 and 562), slightly inclined toward each other, and leaving a small space above an empty space M in the mason-work which supports the plates. The disks D are placed perpendicularly on the plates, and kept separate by wooden wedges, the open part of the floor being closed by sheet-iron plates F, F. Charcoal is heaped between the disks, and the wedges are removed, after which wood is placed in the space M and kindled, the draught being increased by small chimneys o made in the mason-work. As the temperature rises, the lead fuses and runs through a canal a in the floor of the space M, into a crucible c, whence it is run into moulds of a lenticular shape. The copper, still alloyed with a certain quantity of lead, remains on the floor in the form of a half-melted, spongy mass, while the lead which separates by eliquation contains nearly all the silver, which is afterward separated by cupellation.

As the cupreous masses may still yield a certain quantity of argentiferous lead, if the temperature be raised, they are heated in a peculiar furnace, called a *sweating-furnace*, of which fig. 564 represents a vertical section through the line CD of the plane (fig. 565), while fig. 565 shows a horizontal section at the height of the line AB (fig. 564); and lastly, fig. 563 exhibits a front view of the same. The cupreous masses are placed on the floor of the furnace above the strainers F, F, which are filled with wood; when the door of the furnace is closed and the fuel kindled, the draught being assisted by small holes o, o, which open into a chimney H. An additional quantity of lead separates by eliquation; but as the air in the furnace is very oxidizing, the greater portion of this lead is converted into litharge, which falls

to the bottom of the strainers F. A small quantity of oxide of copper also oxidizes, but remains dissolved in the litharge.

There will be, therefore, on the floor, black copper which has lost the greater proportion of the lead and silver it retained, and argenteriferous litharge rich in copper, which are thrown as plumbeous material into the elbow-furnace in which the black copper is smelted with lead, for the preparation of disks for eliquation.

§ 1068. The black copper produced by eliquation is refined in a reverberatory resembling a cupelling furnace, of which fig. 566 represents a vertical section through the line YX of the plane (fig. 567), while fig. 567 gives a horizontal section through the line VU of fig. 566. Wood is burned on the grate F, and the flame passes through the furnace A into the chimney C.

The copper to be refined is placed on the hearth-sole of the furnace, made of moistened charcoal solidly pounded; the charging being done through an opening D, which is afterward closed by a door. When the metal is fused, the wind of

Fig. 563.

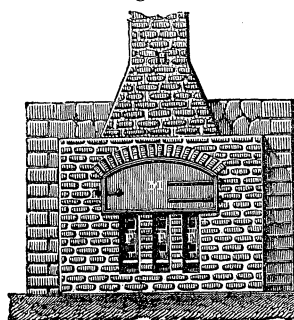


Fig. 564.

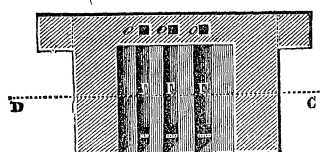
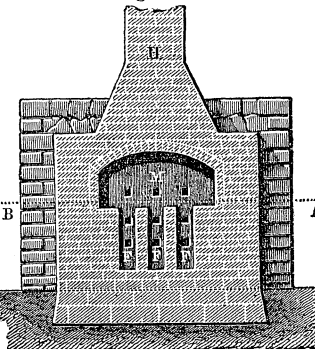


Fig. 565.

Fig. 566.

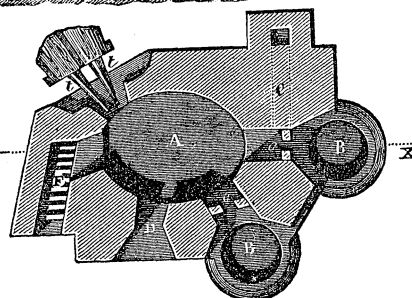
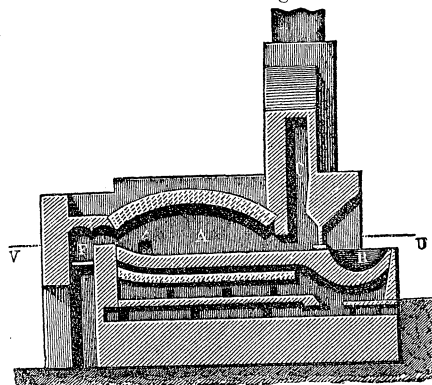


Fig. 567.

two twyers *t* is allowed to blow over the surface of the bath, by the oxidizing action of which the sulphur, lead, and iron first oxidize, while scoriæ and skimmings are formed, which are removed through the door A. After a certain time, the copper has lost its foreign metals, and red scoriæ, very rich in suboxide of copper  $\text{Cu}_2\text{O}$ , are formed. The workman judges of the progress of the operation by plunging an iron rod from time to time into the bath of metal, thus taking out a thimble of copper, which he hammers to ascertain its physical qualities. When the refining is finished, he runs the metal into the basins B, B', pours into them a small quantity of water to solidify the superficial stratum, which he immediately removes, and so on, until he has removed all the copper. The metallic disks are called *rosettes*. In this state the copper is not malleable, as a small quantity of suboxide of copper  $\text{Cu}_2\text{O}$ , which it always contains, destroys this property.

Black copper is frequently refined, in this way, before being subjected to eliquation; but it is not carried so far, and the partially refined black copper is run into cold water, which reduces it to the state of grains or drops. The granulated metal is then fused with the plumbeous material in the elbow-furnace, by which more homogeneous alloys of copper and lead are obtained, than when disks of black copper are fused with lead. After eliquation and sweating, the cupreous material is refined by a process presently to be described.

The process by *amalgamation* will be described in treating of the metallurgy of silver.\*

§ 1069. When black copper contains no silver, it is not subjected to eliquation, but is generally refined in a *refining-furnace*, a vertical section of which is seen in fig. 568, and a perspective view in fig. 569. It is composed of a hemispherical crucible C, of a radius

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\* A recently introduced process of extracting the silver from cupreous matts is now employed to great advantage in Swansea, South Wales, and at several places in Germany. The manipulations are as yet kept secret, while the successive operations are as follows:—The second or third cupreous matt, after having been granulated, or stamped, and reduced to an impalpable powder, is roasted in a reverberatory until all the sulphate of copper formed is decomposed, and the sulphuric acid is completely expelled. The roasted substance is again powdered, and roasted with a certain quantity of common salt, the chlorine of which combines with the silver to form chloride of silver. The product resulting from this operation is sieved; and while the coarser particles, which consist of imperfectly roasted matt which has sintered together, are again roasted with common salt, the powder which has passed through the sieve is treated with a boiling saturated solution of common salt, which dissolves the chloride of silver. The silver is precipitated from its solution in the metallic state by pieces of metallic copper, while the copper in solution is in its turn precipitated by iron. The more perfectly the first roasting was effected, *i. e.* the less sulphuric acid was allowed to remain, the less chloride of copper will form by the subsequent roasting with common salt; and the less copper the solution of silver contains, the more perfectly will the silver be precipitated, and consequently, the more economical will the operation be. The whole process requires great care.—*W. L. F.*

of about 0.2 m. lined with brasque made of 2 parts of charcoal and 1 of clay. It is surrounded by an edge having an opening A, closed by a door, the object of which is to more readily support the charcoal. When first made, or repaired, it is dried for several hours, by filling it with burning charcoal; and, fresh charcoal being added, the pieces of black copper are placed on the side opposite to the twyer T, and the blast is admitted. When the charge of black copper is melted, fresh is added, taking care to always keep the furnace filled with charcoal. A tap-hole *ii'*, allows the escape of the scoriæ which form during the refining. Sulphurous acid, and white vapours of oxide of antimony, when this metal exists in the black copper, are disengaged, while the first scoriæ contain a

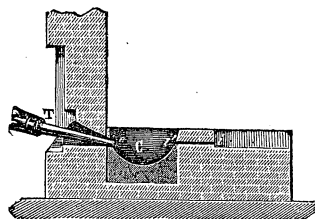


Fig. 568.

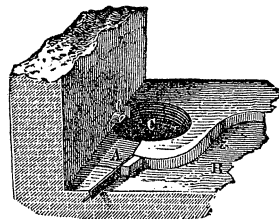


Fig. 569.

considerable amount of oxide of iron, which gives them a greenish hue, while the succeeding slag is of a deep red colour, and very rich in oxide of copper. When the workman has melted the quantity of black copper intended for a single operation, he takes, from time to time, a thimble of copper on the end of an iron rod, and judges, by the appearance of the metal, of the progress of the operation. When he thinks the refining is terminated, he stops the blast, throws a bucket-full of water on the hearth, removes the charcoal, uncovers the surface of the metallic bath, and skims off the supernatant scoriæ; and when its surface is clean, throws on it a small quantity of water to consolidate its superficial stratum, and immediately removes it in the form of a rosette. Water is again poured on, a second rosette removed, and so on, until the operation is terminated. The process generally lasts two hours, and produces a loss of about 25 per cent. on black copper, furnishing 75 per cent. of rosette copper.

§ 1070. Rosette copper does not possess the malleability of the copper of commerce, and, in order to give it the desired properties, must be subjected to a very delicate operation, requiring a skilful workman. The rosettes are remelted in a small furnace, resembling that of figs. 568 and 569, for refining black copper, and, when the fused metal has run into the crucible, it is covered with fine charcoal, when, after some time, all the suboxide of copper is reduced, and the metal has attained its greatest degree of mallea-

bility. But if the workman does not seize exactly the proper moment, the metal again loses its malleability by combining with a small quantity of carbon. When this happens, (which the refiner soon discovers by occasional experiment,) he uncovers the metal, and allows the air of the twyer to play for a few moments over the surface of the bath, which operation he repeats until he attains the favourable period. The purified metal is then run into moulds of various shapes and sizes.

§ 1071. England alone manufactures more than half of the copper used in the world. The most important copper-mines are in Devonshire and Cornwall, while the principal smelting-works are in Wales, and smelt, besides the British ores, many foreign ores coming from Chili, Peru, Cuba, New Zealand, Algiers, Norway, &c.

The ores smelted in the Welsh copper-works may be divided into several classes, according to their richness in copper and their chemical composition:

1. Copper pyrites, mixed with a large proportion of iron pyrites, and containing but a small quantity of oxidized cupreous substances, and accompanied by a quartzose and earthy gangue of little value. They contain from 3 to 15 per cent. of copper.

2. Copper pyrites, presenting the same composition as the foregoing, but containing from 15 to 25 per cent. of copper.

3. Copper pyrites, containing very little iron pyrites and matter injurious to the quality of the copper, but in larger proportion of oxidized cupreous substances, and the gangue of which is essentially quartzose, while they yield from 12 to 20 per cent. of copper.

4. Ores composed principally of oxidized copper-ores, mixed with pyritous and variegated copper. Their gangue is quartzose, and they contain from 25 to 45 per cent. of copper.

5. Very rich oxidized ores, free from sulphides and injurious substances, accompanied by a quartzose gangue, and containing from 60 to 80 per cent. of copper, in the metallic state, and in that of suboxide or carbonate. This valuable ore is imported chiefly from Chili.

§ 1072. The metallurgic treatment begins with ores of the first class, which are roasted in large reverberatory furnaces, a horizontal section of one of which is represented in fig. 571, while fig. 570 shows a vertical section through the line XY in fig. 571. The hearth-sole of this furnace is 21 feet in length by 21 in width, and made of refractory bricks. The vaulted roof descends rapidly from the grate F to the flue R, which conveys the gases into a tall chimney. Four doors *p* on the sides of the furnace serve as working-holes, while an opening *o* near the fire-bridge or *altar*, serves for the introduction of a certain quantity of fresh air, which can be regulated by a register. The hearth-sole has four

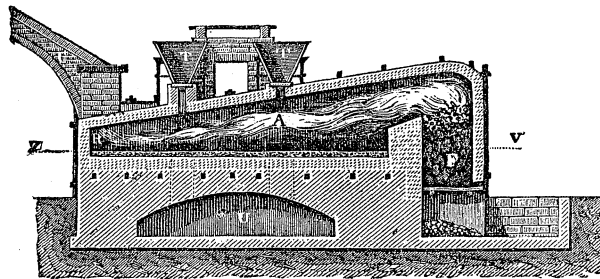


Fig. 570.

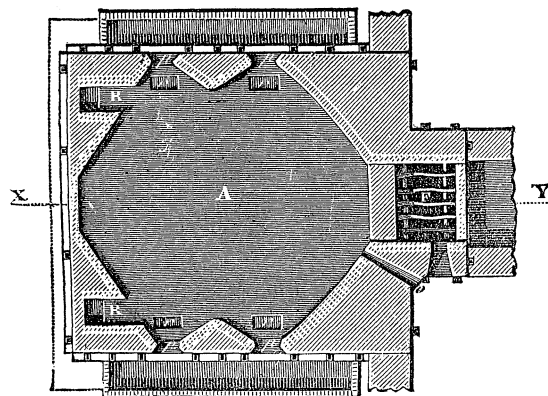


Fig. 571.

rectangular apertures *r* immediately against the working-doors, serving for the extraction of the roasted material, and which are kept closed during the roasting, by cast-iron plates. In the vaulted roof are two large sheet-iron hoppers, through which the ore to be roasted is introduced, and which are provided with registers which on being opened allow the material to fall on the hearth-sole.

The combustible employed for the roasting and smelting is the Welsh anthracite, which, as it burns with difficulty, and is reduced to dust by the influence of heat, cannot furnish, under ordinary circumstances, the necessary flame to heat a reverberatory of 21 feet in length throughout the whole of its extent; and which, moreover, cannot be burned on a common grate, as it would either fall through between the bars, or completely fill up the interstices. These inconveniences have been remedied in a very ingenious way, by which the manner of combustion is rendered different from that generally taking place in reverberatories. The anthracite leaves, on being burned at a high temperature, an ash which by

fusion is rendered pasty, and constitutes a vitreous slag, a property which the workmen make use of to obtain a kind of earthy grate, which is supported only by a few bars of iron, placed wide apart. Different-sized fragments of this slag are heaped on the bars, until the layer has attained the thickness of about 1 or  $1\frac{1}{2}$  feet, after which the ash of the fuel burned on this support forms a kind of slag, which encloses numerous pieces of coal; and when the slag, owing to the accumulation of a fresh quantity above, becomes further removed from the source of heat, it cools, and thus forms new interstices, large enough to allow the current of air necessary for the combustion to pass, but too narrow to permit the escape of powdered fuel. The workman contrives to keep the thickness of the layer of slag uniform, by breaking away pieces from below from time to time, and allowing them to fall into the ash-pit.

About  $\frac{1}{4}$  of its weight of bituminous coal, in small pieces, is added to the anthracite, in order that the former, by adhering to the anthracite, and swelling by the heat, may maintain the desired porosity throughout the mass. The thickness of the layer of anthracite is about 1 foot above the support of slags. The air traverses the layer at innumerable points, and its oxygen is entirely converted into carbonic oxide, which, with the nitrogen, enters the furnace, where it is consumed at the expense of the cold air introduced through the aperture *o* and through the small holes in the working-doors. The whole of the inside of the furnace is thus filled with a long flame of carbonic oxide, which burns by contact with jets of air containing an excess of oxygen, and which spread out like a sheet on the floor of the furnace, because they enter through holes pierced as low as possible.

The ore spread out on the floor of the furnace is thus constantly exposed to a layer of oxidizing air, near a mass of combustible gas which is consumed slowly on its under surface, thus furnishing the heat necessary to the roasting. The roasting of a charge of ore is commenced immediately after the former charge has been extracted, without allowing the furnace to rest. Each charge consists of  $3\frac{1}{2}$  tons, which are introduced by opening the valves of the hoppers in which the ore has been previously heaped; and the workmen immediately spread the whole charge uniformly over the floor, by means of iron rakes, introduced through the four working-holes, which are afterward closed. Every 2 hours a fresh surface is exposed by stirring with long iron poles; and the whole roasting lasts 12 hours. In order to extract the roasted ore, the workmen open the working-doors, and lift up the cast-iron plates which cover the openings *r*, into which they rake the ore, thus causing it to pass into a reservoir *U* under the furnace, whence other workmen take it, after it has cooled, to the smelting-furnace.

§ 1073. The smelting-furnace is a reverberatory, fed by a

mixture of  $\frac{2}{3}$  of anthracite and  $\frac{1}{3}$  of fine pit-coal, which are burned on a bed of scoriæ, the flame being produced by the combustion of the carbonic oxide gas which forms in the stratum of fuel. By forcing the draught a higher temperature can be attained than in the roasting-furnace. Fig. 573 represents a horizontal, and fig. 572 a vertical section of the furnace. The hearth-sole is made of scoriæ, having a depression at B, constituting a kind of inner basin. The roasted ores are smelted by adding to them the rich

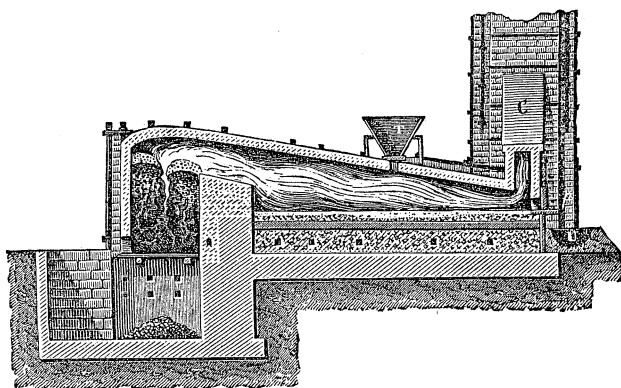


Fig. 572.

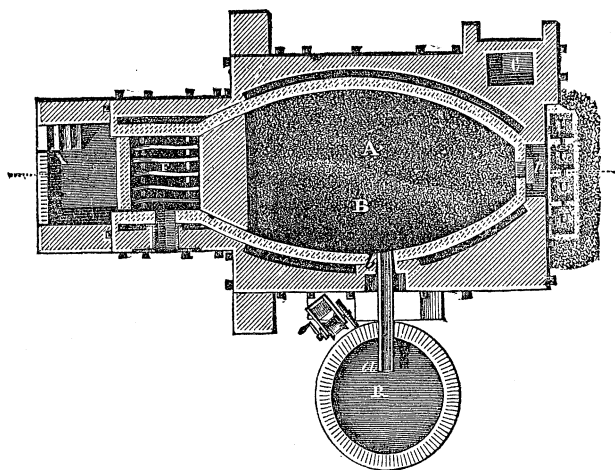


Fig. 573.

scoriæ arising from the preceding operations and unroasted crude ores belonging to the third class; a certain quantity of fluor-spar being added, to give fluidity to the scoriæ. Influenced by the high temperature, the oxides and sulphides react upon each other,



and while the copper combines chiefly with the sulphur, the iron selects the oxygen and passes into the scoriæ. There is, moreover, a reaction between the oxygen of the oxides and the sulphur of the sulphides, and, consequently, disengagement of sulphurous acid. The operation is terminated in 4 hours, and the products of smelting are—a matt which contains the greater portion of the copper combined with the sulphur and a certain quantity of sulphide of iron; and a slag highly charged with oxide of iron, and containing many fragments of quartz, giving it a muddy consistence. The workman draws out the slag, by means of his rake, which he introduces through the working-hole *p* near the flue, and causes the slag to fall into rectangular cavities *U*, made in the same, the shape of which it assumes. At the same time, the smelter opens a tap-hole which penetrates to the bottom of the inner reservoir *B*, when the matt flows in a small stream, and is conducted by a canal *ab* into a reservoir *R* filled with water, when it is divided into very small grains.

The matt arising from this smelting is called *coarse metal*, and contains about 33 per cent. of copper. The scoriæ are broken up, and the pieces sorted; the richest being kept to be added to another smelting of roasted ore, while the remainder is rejected.\*

§ 1074. The coarse metal is then roasted, and again smelted. As the substance has lost the greater part of its sulphur during the roasting, it is not to be prevented that a certain portion of copper should pass into the slag, in the state of oxide, which is, however, of no importance, as the scoriæ must pass through other operations. The furnaces for roasting the coarse metal resemble those for roasting the ore, and the process is similarly conducted, with the exception that toward the close of the operation the temperature is raised higher. The charge is  $4\frac{1}{2}$  tons, and the roasting lasts 36 hours, during which time the material must be frequently turned with a rake. The roasted substance falls through the working-holes *r*.

The roasted coarse metal is smelted with the copper ore of the fourth class, scoriæ very rich in copper arising from the refining of the crude copper, as will be hereafter described, and the scales from the rollers being added. The smelting-furnace resembles that for smelting roasted ores, but the hearth has no inner reser-

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\* The rich slag is separated from the poorer portions in an ingenious manner:—The slag being run out from the furnace into rectangular cavities, and thus obtained in blocks of about  $2\frac{1}{2}$  feet by  $1\frac{1}{2}$ , by 1 in depth, is removed before it has solidified, but not before an outer crust of a certain thickness has formed, and set up in a slanting position, the side which lay undermost in the pit, and which consequently contains all the grains of matt, which, by their greater specific gravity, occupy the lowest position, now forming the upper surface. The cake is then tapped at both ends, when the liquid interior, which is poor in copper, flowing out, leaves a hollow box of slag, the upper side of which is broken out and used, while the other parts are rejected.—*W. L. F.*

voir. The fire is managed in the same way, but a higher temperature is produced, and the operation lasts 2 hours longer. It is endeavoured to mix the materials in such proportions that the sulphide of iron in the smelting-bed may be oxidized by the oxygen of the metallic oxides, and pass nearly wholly into the slag, while the copper combines with the superfluous sulphur to form the matt. The materials react upon each other principally after fusion, the reaction being almost entirely limited to a double decomposition between the sulphide of iron and the oxide of copper, while very little sulphurous acid is disengaged. Toward the close of the operation, the workman stirs the mass with his rod, and then blows up the fire in order to properly separate them; after which he opens the tap-hole, when the matt runs out first, and is received in small canals, while it is followed by the fluid slag. The latter is separated into 2 parts, and while the richest are reserved for special treatment, which yields copper of the first quality, the poorest are added to a new smelting of roasted coarse metal.

The matt is of a grayish-white colour, sometimes slightly bluish, and is called *fine metal*. It contains about 73 per cent. of copper, and resembles in composition the sulphide of copper  $\text{Cu}_2\text{S}$ , although it is rarely entirely free from sulphide of iron.

The rich scorix arising from this smelting are subjected, as we have before said, to a special treatment, being smelted in a reverberatory furnace with a certain quantity of crude ores of class No. 3, which contain but few injurious substances, and sulphur sufficient to transform the copper of the smelting-bed into sulphide, which passes into a matt, which is then treated like the ordinary matts.

§ 1075. The fine metal is subjected to an operation of which the object is to ultimately expel, in the form of sulphurous acid, the sulphur which, until then, had been preserved as an agent of concentration for the copper, and to drive off, at the same time, either by gasification by the assistance of oxygen alone, or by scorification by the united aid of oxygen and siliceous matters, such as arsenic, iron, nickel, cobalt, tin, &c. This is effected by means of two successive reactions which take place in the same furnace: first, by the direct action of the air on the material kept at a temperature near its fusing point, and liquefying drop by drop, which operation is the *roasting* of the matt; and secondly, by the reaction of the oxide of copper, which is formed in great excess, on the sulphides which are not decomposed by roasting. The two products of the operation are *coarse* or *blistered copper*, which is purer than the black copper of the continental manufactories, and a very rich scorix, which is passed through the smelting of the roasted coarse metal.

This process is carried on in a reverberatory furnace resembling other smelting-furnaces, but having a side-door through which the

matt is charged. The matt is in pretty large cakes, which are heaped upon the hearth-sole, while the rich oxidized ores of the fifth class are added; the charge being about 3 tons. In half an hour the matt begins to fuse, and the first liquid drops fall upon the sole, which process lasts about 4 hours; after which all the materials are collected on the sole in a semi-doughy state, when a strong bubbling is observed, owing to the disengagement of sulphurous acid produced by the reaction of the oxides on the sulphides. The temperature is allowed to fall, so as to prolong this reaction until the twelfth hour, at which period the disengagement of sulphurous acid ceases, because the temperature has greatly fallen. The fire is then blown up, the materials become more fluid, and the reaction is completed. In 18 hours, reckoning from the commencement of the operation, the material contains but little sulphur, and the smelter then raises the temperature as high as possible, in order to assist the separation of the substances. In 24 hours he skims the bath with his rake, and runs off the coarse copper into thin cakes, the surface of which is covered with blisters. The scoriæ contain about 20 per cent. of copper.\*

§ 1076. Blistered copper is *refined* without the admixture of any other substance, the reagents being atmospheric oxygen, the siliceous material of the sole and sides of the furnace, and that furnished by the sand, adhering to the cakes of copper. The refining-furnace differs but slightly from other smelting-furnaces, the grate being merely deeper, in order to accommodate more fuel, and its capacity being more ample. As much as 10 tons of blistered copper are charged on the sole, arranged in a heap rising as high as the vault of the furnace. The process lasts 24 hours, comprising the time necessary for charging; but, during the first 18 hours, the workman attends only to the fire. The copper melts gradually under the oxidizing influence of the air, and the oxide of copper thus formed reacts, either immediately, or by combination with the silex, on substances more oxidizable than copper, while a slag is formed, into which, in addition to suboxide of copper  $\text{Cu}_2\text{O}$  in great excess, the oxides of all the other foreign metals enter.

In 22 hours, the copper is completely freed from the sulphur and foreign metals, and the workman then skims the bath and removes all the scoriæ from its surface.

The copper is then in the same state as the rosette copper of the continental foundries, and contains a certain quantity of oxide of copper, which destroys its malleability; but it is obtained

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\* In most of the Welsh copper-works the *fine metal* is subjected to a third successive roasting and smelting, from which there results a matt which in this case is called *coarse copper*, while the product arising from the operations described in this section is called *blistered copper*.

directly in a malleable state in the English works by the following process:—Four or five shovelfuls of charcoal are thrown on the bath, which spread immediately over its whole surface, and then a long stick of green wood is plunged into the bath. In consequence of the elevated temperature to which it is suddenly subjected, the wood disengages reducing gases, which cause the metallic bath to bubble strongly, and considerably hasten the effect which would be ultimately produced by the charcoal on the surface. After twenty minutes of this bubbling, the refiner tests the copper by means of a small mould fastened to an iron rod: he dips out a small sample of copper, places it on an anvil, and tests its malleability by striking it with a hammer. When he is satisfied with its quality, he makes a last skimming and removes the balance of the charcoal and the small quantity of scoriæ which has formed, and then runs the copper into moulds.

#### COPPER OF CEMENTATION.

§ 1077. The water of copper-mines, or that flowing from the washing of roasted copper-ores, often contains a large quantity of sulphate of copper, which is separated by precipitating it by metallic iron. The water is conveyed into large basins, in which iron bars, plates of sheet-iron, or scrap-iron, are placed, on which the copper precipitates in the form of a crystalline powder, while an equivalent quantity of iron dissolves. The copper thus obtained is called *copper of cementation*, (*cuivre de ciment*,) and is refined as above described.\*

#### ALLOYS.

##### *Alloys of Copper and Zinc.*

§ 1078. Pure copper is moulded with difficulty, because it is often filled with flaws and air-bubbles, which spoil the casting; but by alloying it with a certain quantity of zinc, a metal is obtained free from this objection, harder, and more easily worked in the lathe. Zinc renders the colour of copper more pale; and when it exists in certain proportions in the alloy, it communicates to it a yellow hue, resembling that of gold; but when present in larger quantity, the colour is a bright yellow; and lastly, when the zinc predominates, the alloy becomes of a grayish white. Various names are given to these different alloys. The one most used in the arts is *brass*, or

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\* A similar method is employed at Stadtberg, in Westphalia, and on Anglesea, England, to extract copper from carbonated ores; the latter being heaped in large pits, and covered with water, while sulphuric acid, generated on the spot by burning sulphur and a small quantity of nitre in a small furnace with a closed top, is led into the pits, and gradually converts the copper entirely into sulphate. When the mother liquid has become neutral, it is pumped off, and the copper is precipitated from it by scraps of iron.

The same method would probably apply to the working of the large blocks of copper found at Lake Superior.—*W. L. F.*

*yellow copper*, composed of about  $\frac{2}{3}$  of copper and  $\frac{1}{3}$  of zinc. Other alloys are also known in commerce, by the names of *tombac*, *similar* or *Mannheim gold*, *pinchbeck* or *prince's metal*, (chrysocale,) etc.: they contain in addition greater or less quantities of tin.

Tombac, used for ornamental objects which are intended to be gilded, contains 10 to 14 per cent. of zinc; the composition of *Dutch gold*, which can be hammered into very thin sheets, being nearly the same. Similar, or Mannheim gold, contains 10 to 12 per cent. of zinc, and 6 to 8 of tin; and pinchbeck contains 6 to 8 per cent. of zinc, and 6 of tin. The statues in the park of Versailles are made of the following alloy:

Copper .....	91
Zinc.....	6
Tin.....	2
Lead .....	1

The alloys of copper and zinc are altered by a high temperature and a portion of the zinc is volatilized. If brass be heated in a brasqued crucible in a forge-fire, the zinc is nearly wholly driven off.

Brass is made by melting directly copper and zinc; rosette copper being used, fused in a crucible, and run into water to granulate it. The zinc is broken into small pieces. The fusion is effected in

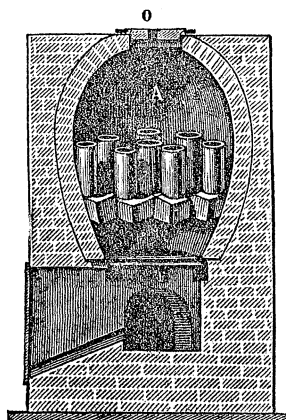


Fig. 574.

earthen crucibles which can contain from 30 to 40 pounds of alloy, the metals being introduced in the proportion of  $\frac{2}{3}$  of copper and  $\frac{1}{3}$  of zinc, to which scraps of brass are added. A certain number of crucibles are placed in an egg-shaped furnace A, (fig. 574,) lined with refractory bricks, and supported by a brick dome, having apertures through which the flame of the fuel passes, the grate F being immediately beneath the dome. The crucibles are introduced through the upper opening of the furnace, which is covered, during the smelting, by a lid having a hole O for the escape of the gases. A register beneath the grate regulates the draught, and serves for the extraction of the crucibles.

When the alloy is fused, the crucibles are removed with tongs, and the brass run into clay moulds; and, sometimes it is run between two very smooth slabs of granite, kept at a proper distance from each other by iron rods.

Small quantities of lead and tin are frequently added to brass to make the alloy harder and more easily worked: brass which contains no lead soon *chokes* a file, which defect is remedied by the addition of 1 or 2 hundredths of lead.

## ALLOYS OF COPPER AND TIN.

§ 1079. Copper and tin mix in various proportions, and form alloys which differ vastly in appearance and physical properties, as tin imparts a great degree of hardness to copper. Before the ancients became acquainted with iron and steel, they made their arms and cutting instruments of *bronze*, composed of copper and tin.

Copper and tin, however, combine with difficulty, and their union is never very perfect. By heating their alloys gradually and slowly to the fusing point, a large portion of the tin will separate by eliquation, which effect also occurs when the melted alloys solidify slowly, causing circumstances of serious embarrassment in casting large pieces.

Different names are given to the alloys of copper and tin, according to their composition and uses: they are called *bronze* or *brass*, *cannon metal*, *bell metal*, *telescope-speculum metal*, etc. All these alloys have one remarkable property: they become hard and, frequently, brittle, when slowly cooled; while they are, on the contrary, malleable, when they are plunged into cold water, after having been heated to redness. Tempering produces, therefore, in these alloys an effect precisely opposite to that produced on steel.

When alloys of copper and tin are melted in the air, the tin oxidizes more rapidly than the copper, and pure copper may be separated by continuing the roasting for a sufficient length of time.

The following are the principal alloys of copper and tin:

Cannon metal, which in France is thus composed:

Copper.....	100	.....	90.09
Tin.....	11	.....	0.91
	111		100.00

Bell metal, which contains

Copper .....	78
Tin .....	22
	100

Cymbal and tam-tam metal, composed of

Copper .....	80
Tin.....	20
	100

Telescope-speculum metal, made of

Copper .....	67
Tin.....	33
	100

Bronze for medals varies slightly in its composition, and generally consists of

Copper .....	95
Tin.....	5
Zinc.....	some thousandths.

VOL. II.—X

Bronze used for the manufacture of ornamental objects generally contains larger quantities of zinc. A portion of the small French coin is made of alloys of copper and tin; and although the red "sous" consist of nearly pure copper, the yellow "sous," coined under the Republic, from a metal obtained by melting the bells, contain on an average 86 of copper and 14 of tin. Other "sous" made during the Republic, with refined bell-metal, are composed of 96 of copper and 4 of tin.

*Cannon-casting.*

§ 1080. Gun-metal must fulfil several important conditions. It should be very tenacious, that the pieces may not burst under the enormous pressure caused by the explosion of the powder, while it should be sufficiently hard not to be injured by the ball, which strikes the sides several times before leaving the muzzle; and, lastly, it should be fusible, because large guns can only be made by casting.

Copper and iron are the only metals which possess sufficient tenacity; but as pure iron will not fuse very readily, it is necessary to substitute for it cast-iron, the tenacity of which is much inferior. Copper possesses great tenacity, but is too soft; and, in rapid service, would soon be so battered as to be useless. Recourse must then be had to alloys of copper with other metals; and long experience has shown that alloys of copper and tin are the most suitable; but as, while tin greatly increases the hardness of copper, it diminishes its tenacity, it becomes necessary to stop at certain proportions of the two metals, at which the alloy possesses both the requisite degree of hardness and tenacity. These proportions, which have been determined by numerous experiments, made at various times and in different countries, have been fixed at 11 of tin for 100 of copper. It has, however, been ascertained, that for pieces of a calibre below 8, an alloy of 8 or 9 per cent. of tin is preferable. Many experiments have also been made to ascertain if the alloy could not be improved by the addition of other metals, as zinc, iron, or lead; but these complicated alloys have all been rejected, on account of the great variation of their results; and pieces were frequently rendered useless in consequence of the difficulty of obtaining such alloys homogeneous and of uniform composition.

The use of cast-iron for the manufacture of cannon is long subsequent to that of brass. As it is cheaper, it might be very advantageously substituted for bronze, but it is very brittle, and pieces of the same calibre must be much thicker than of the latter metal, thus becoming too ponderous for field-service. They are well adapted to stationary batteries, fortifications, coast defence, and ships of war. Cast-iron guns ring much less than those of bronze, and, for this reason, are preferable on board of ships, where brass pieces, on the lower-deck batteries, would make a noise insupportable by the gun-

ners. Very soft cast-iron, made with charcoal, should alone be used for artillery; and some of the Swedish iron is highly valued for this purpose.

The furnaces in which bronze is melted should contain no oxidizing gases, and the atmospheric air traversing them should be deprived by combustion, as far as possible, of its oxygen, because the tin, which is more oxidizable than copper, would constantly separate from the alloy in the form of oxide, and the composition of the bronze, at the time of casting, would not be known with certainty.

Figs. 575 and 576 represent a melting-furnace, used in the cannon-foundry at Toulouse. It is a circular reverberatory furnace A, with a surbased dome, heated by the grate F, on which small billets of wood are burned. The wood being charged through the

Fig. 575.

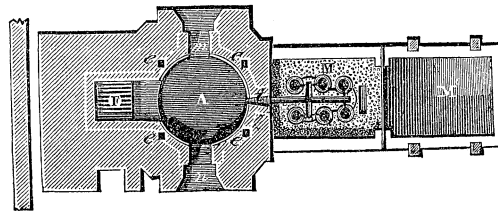
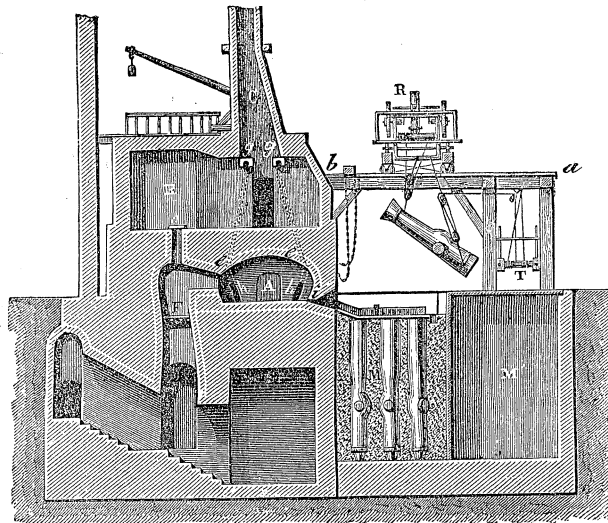


Fig. 576.

opening *o*, a thick layer of fuel is heaped on the grate, in order that the atmospheric air, which does not enter the furnace until it has passed through the fuel, shall be completely deprived of its oxygen. The draught is regulated by 4 elongated working-holes *h, h*, arising



from the hearth-sole and terminating at the vent-holes *eg, eg*, which open into the chimney C, by means of which arrangement the flame is obliged to spread over the metallic bath which covers the hearth-sole. Near the furnace are cavities M, M', lined with cement to preserve them from dampness, and in which the moulds are placed, and kept firm by heaping earth around them. The moulds, which are made of clay, cow's-hair, and horse-dung, intimately mixed, are fashioned on a model in relief, partly of earth and partly of plaster, which is destroyed when the mould is finished, and strengthened by iron bands or loops. Above the mouth of the gun is a prolongation, called the *masselotte*, or lump, the use of which will soon be explained. The moulds, after being baked at a high temperature, so as to dry them as much as possible, are fixed in their places, the breech being downward. Between the tap-hole *i* and the moulds, canals are made which convey the liquid bronze into each mould; and above is a railway *ab*, with a car R, containing a capstan, by means of which the moulds, when filled, can be lifted out and carried away.

Moulding-sand, so well adapted to the moulding of cast-iron and other metals, has been substituted for the earth with which the moulds are made, but never with success, as the walls of the sand-mould are too compact and too impervious to gases. Now, immediately after the casting of bronze, the metal disengages numerous gaseous bubbles, which pass through the porous walls of the mould, and present less resistance than the high column of melted metal; while in the sand-moulds, the gases not being able to escape through the sides, produce a constant bubbling in the mass, giving rise to numerous flaws, and assisting the separation, by eliquation, of the tin, or alloys rich in tin.

The charge of a furnace is composed of old brass, chiefly condemned cannons, and *masselottes* taken from pieces previously cast, with brass turnings taken from the lathe or the boring-machine, and a certain quantity of new metals, copper and tin, besides *white metals*, or alloys very rich in tin, which separate by eliquation in the moulds. The proportions of copper and tin in the several components being determined by analysis, they are mixed in the proportion of 100 copper to 13 or 14 tin, which is reduced by oxidation of tin in the furnace to the normal proportion of 100 : 11.

The condemned cannons and *masselottes* are laid on the hearth-sole, near the bridge, where the temperature is highest; while the copper, which should be very pure, in bars, and the turnings, are placed thereon, the white metals and tin being added at a later period. In 6 or 7 hours the mass is almost entirely fused, and the flame escapes by every avenue. The smelter first stirs the material with sticks of very dry wood, and draws the portions which are not melted toward the bridge; after which he completes the charge by adding the white metals and tin, which he runs in the form of pigs

into different parts of the bath. He stirs it a second time, in order to render it homogeneous, and, after skimming off the superabundant scoræ, closes the doors of the furnace and blows up the fire, to bring the alloy to a proper state of liquidity; stirs and skims it a third time, and then opens the tap-hole. Other workmen direct the melted metal into each mould.

A remarkable phenomenon ensues in a few moments after the casting. A bubbling takes place in the upper part of the mould, proportioned to the size of the piece and the elevation of temperature, and a portion of the bronze rises in the form of a mushroom, being an alloy much richer in tin than the cast metal. A partial eliquation therefore takes place during the cooling, which causes the separation of an alloy more fusible and containing more tin. The composition of the piece itself is not uniform, as the proportion of tin diminishes from the breech to the upper part of the masselotte. The intention of the masselottes is, not only to exert considerable hydrostatic pressure on the lower strata of the piece, but also to furnish metal necessary to compensate for the contraction of the metal by cooling and its loss of substance by eliquation.

Twelve hours after the casting, the earth is cleared away in order to hasten the cooling of the moulds; and the latter are removed after 48 hours, broken, and the cast guns carried to the boring and turning shops.

When the surface of the piece is turned, and it has been bored to a certain point, it is examined to ascertain if it be free from such defects as would render it unserviceable. Such defects are various, and called by different names; but they are nearly all produced by eliquation of the tin or very fusible alloys.

*Flaws*, or *bubbles*, are cavities with smooth surfaces, produced by bubbles of gas which have been unable to escape; while *honeycombs* are cavities with rough surfaces, arising from irregular distribution of the materials or badly proportioned alloy; and *worm-holes* are similar but smaller cavities. *Cendrures* are owing to impurities in the alloy, remaining in the metal, or detached from the sides of the mould; and *tin-spots* are produced by small, very hard masses of an alloy containing 20 or 25 per cent. of tin, which became separated by eliquation, and were unable to ascend as far as the masselotte. *Blasts*, or *cracks*, (sifflets,) which are longitudinal or traverse grooves, sometimes extending through the whole thickness of the piece, are likewise owing to a separation of the tin.

If the piece is found to be perfect, the boring and turning are completed, and it is subsequently examined and proved according to the regulations of the service.

#### TINNING OF COPPER AND BRASS.

§ 1081. The use of copper and brass for culinary purposes is dangerous, on account of the ease with which copper, on oxidizing

x2

by contact with the air and acid substances, forms very poisonous salts, unless the vessels are lined with a coat of tin, which prevents the liquids from coming in contact with the copper. The tinning of copper is effected by cleansing the pieces with chlorohydrate of ammonia, and spreading, with a piece of cloth or tow, melted tin over their surface when properly heated. The tin thus adheres to the copper and covers it completely.

Pins are made of brass wire, and whitened by being covered with a thin coat of tin by the humid way. The pins are first cleansed by heating them in a solution of cream of tartar, and then placed in a copper basin with a solution of cream of tartar and tin. The liquid is boiled for about one hour, when the tin dissolves in the cream of tartar with disengagement of hydrogen gas, and is precipitated on the brass of the pins, covering them with a very thin pellicle of metal.

#### ANALYSIS OF BRASS AND BRONZE.

§ 1082. We have said (§ 1078) that brass is composed of copper and zinc, but that a small quantity of lead and tin is usually added, to make the alloy more easy to work. Cannon-metal is composed of copper and tin alone, but the metal used for ornamental objects and medals contains in addition zinc and frequently lead. We shall therefore consider the more general case, and suppose that the alloy to be analyzed contains copper, zinc, tin, and lead.

The alloy is dissolved in pure nitric acid, which converts the tin into insoluble metastannic acid; while the copper, zinc, and lead are transformed into soluble nitrates. After treatment with water, the metastannic acid is collected on a filter; and the weight of tin in the alloy is inferred from that of the metastannic acid.

The filtered liquid is evaporated to dryness, and sulphuric acid added, which converts the nitrates into sulphates; and then, after having driven off the nitric acid by heat, the residue is dissolved in water, when the sulphate of lead, being insoluble, is separated on a filter and weighed after calcination, the quantity of lead in the alloy being deduced from its weight.

The liquor is then supersaturated with sulphhydric acid gas, which precipitates the copper entirely in the state of sulphide, while the zinc remains in solution, because it is not precipitated by sulphhydric acid in a liquid containing an excess of acid. The sulphide of copper is treated as described, (§ 1059,) and the copper is determined in the state of oxide, by means of the standard solution of sulphide of sodium.

The liquid is boiled in order to drive off the sulphhydric acid, and carbonate of soda is added, which precipitates the zinc in the state of hydrocarbonate, which is collected on a filter and weighed after calcination, the zinc being thus determined in the state of oxide. In very accurate analyses, it is proper to ascertain if the filtered

liquid does not still contain a small quantity of zinc, which often happens, because, when acting on the alloy by nitric acid, ammoniacal salts are frequently formed, which prevent the complete precipitation of the zinc by the alkaline carbonates. In order to be sure of this, the liquid is evaporated to dryness and the residue calcined to drive off the ammonia, when, by treatment with water, the zinc remains in the state of carbonate.

It frequently happens that brass or bronze contains a small quantity of iron, introduced by the fact of impure metals being used in making the alloy. In this case, after having boiled the liquid, the copper of which is precipitated by sulphydric acid, a few pinches of chlorate of potassa must be thrown into the boiling liquid, or a current of chlorine passed through the solution, in order to convert the iron into the sesquioxide. The liquid is saturated by ammonia, and the succinate of ammonia, which precipitates the iron from it, is added. The filtered liquid which contains the zinc, contains too large a proportion of ammoniacal salts to allow this metal to be immediately precipitated by carbonate of soda, for which reason the liquid must be evaporated, the carbonate of soda added, and the substance be perfectly dried. By treating it with water the hydrocarbonate is wholly precipitated.

## MERCURY.

EQUIVALENT = 109 (1250.0; O = 100).

§ 1083. Mercury is the only metal which is liquid at the ordinary temperature. It congeals at temperatures below  $40^{\circ}$ ; and then forms a white, very brilliant metal, resembling silver. Solid mercury is malleable, and flattens under the hammer, so that medals may be struck of it. In the polar regions, mercury frequently congeals from the intense degree of cold; and it may be solidified in a refrigerating mixture of solid carbonic acid and ether, (§ 254,) or in a mixture of ice and chloride of calcium, (§ 374). It is sufficient to use finely pounded ice, cooled below  $32^{\circ}$ , and small crystalline grains of chloride of calcium, such as are obtained by crystallizing a concentrated hot solution, and disturbing the crystallization. By operating on a moderate quantity of mercury, placed in a large crucible, which is gradually cooled in the refrigerating mixture, the metal may be obtained crystallized, if, as soon as a thin crust of solid mercury forms on the sides of the crucible, the liquid portion is poured off; when brilliant regular octohedrons, often clearly terminated, are found on the inside.

The density of solid mercury has been found to be 14.4, at a temperature a little below that of its congelation; while the specific

gravity of the metal in the liquid state is 13.596, at a temperature of  $32^{\circ}$ . Mercury expands, while passing from  $32^{\circ}$  to  $212^{\circ}$ , by a fraction 0.018153 of its volume at  $32^{\circ}$ , or by  $\frac{1}{5506}$  for every degree, which is equal to  $\frac{1}{5506}$  for each centigrade degree. It boils at  $662^{\circ}$  of the air thermometer, and the density of its vapour is 6976. The tension of the vapour of mercury is appreciable at the ordinary temperature, although it is too feeble to be accurately measured; but the volatility of mercury is placed beyond doubt by the action which the metal exerts, at the ordinary temperature and distance, on daguerreotype plates which have been exposed to iodine and affected by light. The globules of mercury which condense in the upper part of the vacuum of barometers, also attest its volatility. At the temperature of  $212^{\circ}$  the tension of mercurial vapour is about  $\frac{1}{2}$  millimetre. By boiling the metal with water, in a glass retort, a considerable quantity of mercury is distilled. Below  $32^{\circ}$  the volatilization of mercury is nearly inappreciable, and its vapour appears to no longer possess the expansive force characterizing elastic fluids. In fact, on suspending a leaf of gold in a bottle containing a small quantity of mercury, and allowing the bottle to rest for several days in a low temperature, the leaf is whitened by the mercurial vapour only to the height of a few centimetres above the surface of the bath, the upper portion always retaining its characteristic yellow colour.

§ 1084. The mercury of commerce is nearly pure when it comes directly from the furnace, while that used in the laboratory almost always contains small quantities of foreign metals and oxide of mercury in solution. After some time, especially in summer, mercury absorbs oxygen from the air; and when the metal is agitated, the oxide is scattered through the whole mass, but, when at rest, rises to the surface and forms a gray pellicle. When mercury is pure, it adheres neither to glass nor to porcelain, but flows freely over its surface; but when it contains foreign matters, or even oxide of mercury, it adheres remarkably, and on rolling it slowly over a glass plate, does not form spherical globules, but drops elongated in the shape of tears, which are wrinkled on their surface, and leave a gray pellicle adhering to the glass: the mercury is then said to *leave a tail*, (*faire une queue*.) The mercury of the laboratory cistern may be greatly purified by passing over the surface of the bath, a very dry, large glass tube, to which the superficial pellicle of gray oxide adheres, and may thus be removed.

Mercury is purified, in the first place, by distillation, which operation is easily effected in the cast-iron bottles in which it is usually transported. One of these bottles being half-filled with mercury, and a curved gun-barrel *abc* introduced into its mouth, the bottle is arranged in a furnace, as represented in fig. 577, and a tube *cd*, formed of several layers of linen and dipping into a pan of water, is attached to the gun-barrel. The end of the latter and the linen

are kept wet by a stream of water flowing constantly; and, lastly, the bottle is heated to the boiling point of mercury, when ebullition takes place with violent bubbling, and the mercury distils over,

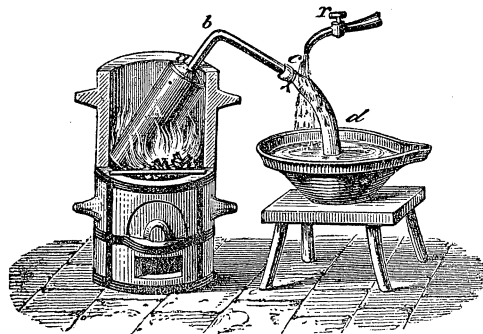


Fig. 577.

leaving the greater proportion of the foreign metals in the bottle. A considerable quantity, however, is carried over by distillation, and it cannot be expected to obtain pure mercury from a single operation. The distilled mercury is placed in a cast-iron receiver, ordinary nitric acid diluted with twice its weight of water is

poured upon it, and it is heated to  $50^{\circ}$  or  $60^{\circ}$ ; when protonitrate of mercury is formed, which, together with the free acid, react on the foreign metals, while the latter dissolve in the acid liquid, the oxide of mercury which may have formed by contact with the air, during distillation, also entering into solution. The acid is allowed to act for at least 24 hours, stirring the mass from time to time; and lastly, it is gently heated to drive off the water, when the nitrate of mercury remains in the form of a crystalline crust, which is removed, and from which the metallic mercury can be extracted. The mercury is washed rapidly in water, and dried, first with tissue paper, and then under a bell-glass with quicklime.

The distillation of mercury frees it so imperfectly from foreign substances that it is rarely useful, and it is in all cases preferable to treat the impure mercury directly with nitric acid and repeat the operation as often as may be necessary.

When mercury merely contains oxide, it is sufficient to place it in a bottle with a small quantity of concentrated sulphuric acid, and to shake it from time to time, in order to bring all its parts into contact with the acid. In 2 or 3 days the acid is poured off and the mercury washed.

After a time, mercury exerts a deleterious action on the animal economy. Workmen in this metal, or those who are frequently exposed to its vapours, are liable to paralysis and copious salivation.

We have mentioned that mercury absorbs, after some time, a small quantity of oxygen from the air, even at the ordinary temperature; but the oxide, mixed with or dissolved in a large quantity of free metal, forms a gray pellicle, which adheres to glass, or the surface of the bath. In order to ascertain that the pellicle contains oxide of mercury, it suffices to distil a certain quantity of it in a current of nitrogen gas, when it deposits a small crystalline residue

of red oxide of mercury. Oxidation advances more rapidly at the boiling point of mercury; and by boiling the metal slowly in a long-necked balloon, into which the air enters freely, a considerable quantity of oxide of mercury can be produced in the form of small, red prismatic crystals. This oxide was originally prepared in this way, and called by the old chemists *precipitate per se*; and it has already been shown (note to § 95, vol. i.) that by keeping mercury for a very long time at a temperature approaching its boiling point, it is possible to determine by approximation the composition of atmospheric air.

Concentrated chlorohydric acid does not sensibly act on mercury even when hot, and dilute sulphuric acid does not attack it; while concentrated hot sulphuric acid soon transforms it into sulphate of mercury, with disengagement of sulphurous acid.

Nitric acid, even when cold, attacks mercury when the acid is dilute, while deutoxide of nitrogen is disengaged.

#### COMPOUNDS OF MERCURY WITH OXYGEN.

§ 1085. Two compounds of mercury with oxygen are known: the less oxygenated, to which we shall give the name of *black-oxide*, or *suboxide of mercury*,\* corresponding to the formula  $\text{Hg}_2\text{O}$ ; while the formula of the more oxygenated, which we shall call *red*, or *protoxide of mercury*, is  $\text{HgO}$ .

*Suboxide of mercury*  $\text{Hg}_2\text{O}$  is not a very fixed compound, but forms with the acids well-defined salts, which crystallize readily. It is obtained by precipitating one of its salts, the nitrate, for example, by caustic potassa, when a black precipitate is formed, which decomposes spontaneously into the red oxide and metallic mercury. By grinding the powder in a mortar for some time, small globules of metallic mercury will be found, which decomposition takes place much more rapidly at the temperature of  $212^\circ$ , or even at the ordinary temperature, when assisted by solar light.

The *protoxide* or *red oxide of mercury*  $\text{HgO}$  is formed when mercury is exposed to the air at a high temperature, which process, however, yields only a small quantity; and it is more easily obtained by decomposing nitrate of mercury by moderate heat. The same oxide is obtained by calcining the subnitrate  $\text{Hg}_2\text{O}, \text{NO}_5$  or the protonitrate  $\text{HgO}, \text{NO}_5$ ; but the product differs slightly in appearance, according to the nature of the nitrate from which it was formed. Thus, the nitrate  $\text{HgO}, \text{NO}_5$  in small crystals, produces crystalline oxide of mercury of a brickdust colour, while the nitrate  $\text{Hg}_2\text{O}, \text{NO}_5$  yields an orange-yellow oxide.

By adding potassa to a solution of protonitrate of mercury

\* The name of *protoxide* is sometimes given to the suboxide of mercury  $\text{Hg}_2\text{O}$ , and that of *binoxide* to the protoxide  $\text{HgO}$ : we shall not adopt this nomenclature, for the reasons given, (§ 1040,) because it does not agree with our chemical formulæ.

$\text{HgO}\cdot\text{NO}_2$ , a yellow precipitate of anhydrous oxide of mercury is obtained.

The red and the yellow oxide of mercury constitute two isomeric states, which are evinced in some chemical reactions. The non-calcined yellow oxide, that is, the oxide obtained by the humid way, is more easily attacked by chlorine than the red oxide, and, when cold, combines with oxalic acid, which under the same circumstances exerts no action on the red oxide.

#### SALTS FORMED BY THE SUBOXIDE OF MERCURY, $\text{Hg}_2\text{O}$ .

§ 1086. The suboxide of mercury  $\text{Hg}_2\text{O}$  forms with the majority of the acids well-defined salts, which are often called *salts of mercury at the minimum*. The subnitrate is obtained by dissolving cold mercury in dilute nitric acid, taking care to keep the mercury in excess; and the subsulphate is prepared by heating mercury in excess with concentrated sulphuric acid. Many salts of mercury at the minimum are prepared by double decomposition.

Suboxide of mercury forms several salts with the same acid; and the neutral salts are colourless when the acid is free from colour, while the basic salts are yellow. The latter are insoluble in water, while the majority of the neutral salts produce colourless solutions. Some neutral salts of the suboxide are decomposed by water into basic salts which are precipitated, and salts with excess of acid which dissolve. These salts are known by the following characters:

The caustic alkalies and ammonia throw down a black precipitate, insoluble in an excess of reagent, and which, when slightly heated, yields globules of metallic mercury. If it be rubbed with a blade of very bright copper, the latter becomes white by being alloyed with the mercury. The alkaline carbonates yield dirty-yellow precipitates which soon turn black.

Prussiate of potash throws down a white precipitate.

Sulphydric acid gives a black precipitate, and the alkaline sulphhydrates yield the same precipitate, which does not dissolve in an excess of the reagent.

Chlorohydric acid and the chlorides throw down a white precipitate of chloride of mercury  $\text{Hg}_2\text{Cl}$ , perfectly insoluble in water and dilute acids.

Iodide of potassium gives a greenish-yellow precipitate, which dissolves in an excess of reagent.

Iron, zinc, and copper precipitate mercury from its solutions, in the state of an amalgam.

#### *Subnitrates of Mercury.*

§ 1087. Suboxide of mercury forms several compounds with nitric acid. The neutral nitrate is obtained by pouring an excess of dilute nitric acid on metallic mercury, and allowing the action to ensue in the cold; when the mercury oxidizes at the expense of the oxygen



of a portion of the nitric acid, and, after some time, large, colourless crystals of subnitrate separate, the formula of which is  $\text{Hg}_2\text{O}, \text{NO}_5 + 2\text{H}\ddot{\text{O}}$ , and which dissolve in a small quantity of cold water, but are decomposed by a large quantity of this fluid, a basic nitrate being precipitated, which may be redissolved by the addition of nitric acid.

If, on the contrary, dilute nitric acid be added to a large excess of metallic mercury, and allowed to react, when cold, for a sufficient length of time, the metal becomes covered with large, colourless crystals, generally well defined, belonging to a basic nitrate, of which the formula is  $3\text{Hg}_2\text{O}, 2\text{NO}_5 + 3\text{H}\ddot{\text{O}}$ . If this salt or the neutral nitrate be treated with tepid water, a bibasic nitrate of the formula  $2\text{Hg}_2\text{O}, \text{NO}_5$  is obtained. By boiling the latter compound with water, it is converted into a green powder, which appears to be a still more basic nitrate.

The neutral nitrate is easily distinguished from the basic nitrates by rubbing them up with a concentrated solution of sea-salt, in which case the neutral nitrate remains colourless, because the mercury passes entirely into the state of chloride  $\text{Hg}_2\text{Cl}$ , while the basic nitrates turn blackish gray, because suboxide of mercury  $\text{Hg}_2\text{O}$  is separated simultaneously with the chloride  $\text{Hg}_2\text{Cl}$ .

When a dilute solution of ammonia is added to an equally dilute solution of subnitrate of mercury, a gray precipitate of the formula  $(\text{NH}_3 + 3\text{Hg}_2\text{O})\text{NO}_5$  is obtained, and which is used in pharmacy under the name of *soluble mercury of Hahnemann*. The composition of this precipitate varies according to the concentration and temperature of the solutions.

#### *Subsulphate of Mercury.*

§ 1088. By adding sulphuric acid to a solution of subnitrate of mercury, the subsulphate is precipitated as a white crystalline powder, which is very slightly soluble in water, one part of the salt requiring 500 parts of cold and 300 of boiling water. It is also obtained by heating concentrated sulphuric acid with a large excess of mercury, but it is difficult to prevent the formation of the protosulphate  $\text{HgO}, \text{SO}_3$ .

#### *Subcarbonate of Mercury.*

§ 1089. By pouring a solution of carbonate of soda into a solution of subnitrate of mercury, a white granular precipitate of the formula  $\text{Hg}_2\text{O}, \text{CO}_2$  is obtained.

#### SALTS OF THE PROTOXIDE OF MERCURY, $\text{HgO}$ .

§ 1090. The neutral salts of the protoxide of mercury  $\text{HgO}$  are colourless, while the basic salts are yellow; and their solutions exhibit the following reactions:

Caustic potassa and soda, in excess, yield a yellow precipitate of

the protoxide, while ammonia in general produces white precipitates, containing ammonia or its elements.

Carbonate of potassa throws down a red precipitate, which does not dissolve in an excess of reagent, and carbonate of ammonia gives a white precipitate.

The alkaline phosphates and arseniates form white precipitates, easily soluble in an excess of acid.

Sulfhydic acid, in small quantity, throws down a white precipitate, which contains, at the same time, sulfhydic acid and the elements of the mercurial salt; while the same acid, in larger quantity, produces an orange precipitate. But if the solution of the mercurial salt be digested with an excess of sulfhydic acid, the precipitate turns black, owing to the forming of sulphide of mercury  $\text{HgS}$ . The alkaline sulfhydrates also yield white or orange precipitates when used in small quantity, and in excess they turn the precipitate black.

Ferrocyanide of potassium throws down with protosalts of mercury in solution a white precipitate, which turns blue after long exposure to the air, the ferrocyanide of mercury being then decomposed; and while soluble simple cyanide of mercury is formed, prussian-blue is separated.

Iodide of potassium gives a beautiful red precipitate, which may dissolve both in an excess of alkaline iodide and in an excess of the mercurial salt, soluble double iodides being formed in both cases.

Chlorohydric acid and the solutions of the soluble chlorides do not precipitate protosalts of mercury, unless their solution be very concentrated; which characteristic distinguishes them from the subsalts of mercury, which yield, in this case, a white precipitate  $\text{Hg}_2\text{Cl}$ , whatever may be the degree of their dilution. In order to ascertain if a mercurial solution contains, at the same time, subsalts and protosalts of mercury, chlorohydric acid is poured into it, when all the mercury which existed in the state of suboxide is precipitated in the form of chloride  $\text{Hg}_2\text{Cl}$ , while that which was in the state of protoxide is dissolved. It is, therefore, sufficient to ascertain if the filtered solution produces a yellow precipitate of protoxide of mercury with potassa, or a red precipitate with iodide of potassium.

#### *Protonitrate of Mercury.*

§ 1091. Protonitrate of mercury is obtained by dissolving mercury, when hot, in an excess of nitric acid, and boiling the salt with nitric acid until no more reddish vapours are disengaged. It may be admitted that the neutral salt exists in the acid solution, but, if the latter be evaporated, it deposits, on cooling, crystals of the basic nitrate  $2\text{HgO}, \text{NO}_5 + 2\text{HO}$ . The neutral nitrate cannot be separated by pouring alcohol into the solution, as the bibasic nitrate is again precipitated. Nevertheless, the solution with an excess of acid, evaporated to the consistence of syrup, deposits crystals of

VOL. II.—Y

neutral nitrate, when kept for some time in a refrigerating mixture. If the preceding nitrates be dissolved in a large quantity of water, they are decomposed, and throw down a white precipitate, of which the formula is  $3\text{HgO}, \text{NO}_3 + \text{HO}$ , and which is remarkable for its great fixedness, for it dissolves with difficulty in nitric and sulphuric acid. Boiled with water, it again gives off acid, and, if the ebullition were sufficiently prolonged, it would probably be converted into an oxide. If a solution of protonitrate of mercury be boiled with metallic mercury, the subnitrate  $\text{Hg}_2\text{O}, \text{NO}_3$  is obtained.

*Protosulphate of Mercury.*

§ 1092. Protosulphate of mercury is obtained by heating metallic mercury with concentrated sulphuric acid in excess, a white crystalline powder being formed. But the evaporation with sulphuric acid must be prolonged until copious vapours of the acid are given off, as, otherwise, the protosulphate of mercury would be mixed with subsulphate. This compound is often prepared in manufactories of chemicals, because it is used in the manufacture of the chloride of mercury  $\text{HgCl}$ , or corrosive sublimate. One part of mercury and slightly more than 1 part of concentrated sulphuric acid are then heated in a glass retort, and when the metallic mercury has disappeared, the heat is still continued in a sand-bath until the product is perfectly dried, when anhydrous sulphate is obtained. It is decomposed, when treated by a large quantity of water, into a yellow basic salt  $3\text{HgO}, \text{SO}_3$ , used in medicine under the name of *turpeth mineral*, and into a salt with a great excess of acid, which crystallizes on the evaporation of the liquid. Turpeth mineral is itself decomposed by being boiled with water, and oxide of mercury is left only at last.

*Protochromates of Mercury.*

§ 1093. Two protochromates of mercury are known, the formulæ of which are  $3\text{HgO}, \text{CrO}_3$  and  $4\text{HgO}, \text{CrO}_3$ . The first is obtained by pouring protonitrate of mercury into a solution of bichromate of potassa, or by boiling the yellow oxide of mercury with the bichromate; it is a brick-red precipitate. The chromate  $4\text{HgO}, \text{CrO}_3$  is obtained by boiling for a long time the red protoxide of mercury with a solution of bichromate of potassa.

*Protocarbonates of Mercury.*

§ 1094. By adding a solution of protonitrate of mercury to a solution of neutral carbonate of potassa in great excess, an ochrous brown precipitate of carbonate of protoxide of mercury is formed, having the formula  $4\text{HgO}, \text{CO}_3$ ; and if the same experiment be made by substituting the bicarbonate for the neutral alkaline carbonate, a brown precipitate of the formula  $3\text{HgO}, \text{CO}_3$  is obtained. The precipitates which are formed when alkaline carbonates are

poured into a solution of nitrate of mercury are very complicated, because subnitrates of mercury are first deposited.

### *Fulminate of Mercury.*

§ 1095. This is a highly explosive compound, consisting of protoxide of mercury united with an acid, *fulminic acid*, formed of cyanogen and oxygen, and of which the formula is  $\text{CyO}$  or  $\text{C}_2\text{NO}$ , and used for the manufacture of percussion caps. Fulminate of mercury is prepared by causing alcohol to react on the acid proto-nitrate. A quantity of mercury is dissolved in 12 parts of nitric acid of  $35^\circ$  or  $40^\circ$  of Baumé, and 11 parts of alcohol at .86 are gradually added to the solution; and, while the temperature is slowly elevated, a lively reaction accompanied by a copious evolution of reddish vapours soon ensues, when the liquid, on cooling, deposits small crystals of a yellowish-white colour.

Fulminate of mercury is one of the most explosive compounds known, and should be handled with great care, especially when it is dry, as it detonates when rubbed against a hard body. It dissolves readily in boiling water, but the greater portion of it is again deposited in crystals during cooling.

The fulminating material of percussion caps is made of fulminate of mercury, prepared as just stated, after having been washed in cold water. The substance is allowed to drain until it contains only about 20 per cent. of water, and is then mixed with  $\frac{2}{3}$  of its weight of nitre, which mixture is ground on a marble table with a muller of guaiacum-wood. A small quantity of the paste is then placed in each copper cap and allowed to dry, the fulminating powder in the cap being often covered with a thin coat of varnish to preserve it from moisture.

### OXIDE OF MERCURY AND AMMONIA.

§ 1096. By treating protoxide of mercury  $\text{HgO}$  with a large excess of perfectly caustic liquid ammonia, a yellow powder is obtained, which must be rapidly washed and dried under a bell-glass with quicklime, and the composition of which is expressed by  $4\text{HgO}, \text{NH}_3 + 2\text{HO}$ , although a more rational formula would be  $3\text{HgO}, \text{HgNH}_2 + 3\text{HO}$ . It is called *oxide of mercury and ammonia*. The preparation of this substance must be effected without access of air, as, otherwise, the compound would soon absorb carbonic acid, and a mixture of oxide of mercury and ammonia with carbonate of the same compound oxide would be obtained; for which purpose, the oxide of mercury is placed in a bottle completely filled with a concentrated solution of perfectly caustic ammonia, and then corked. Either the red or yellow variety of protoxide of mercury may be used, but the red oxide requires a greater length of time. The hydrated oxide of mercury and ammonia, when left for a long time

in a dry vacuum, loses its water; and if it be left until it no longer loses in weight, a brown powder remains, which consists of anhydrous oxide of mercury and ammonia  $3\text{HgO}, \text{HgNH}_2$ . The dishydration takes place very rapidly at a temperature of  $266^\circ$ , without any decomposition of the substance.

The hydrated oxide of mercury and ammonia is insoluble in water and in alcohol. A cold solution of caustic potassa exerts scarcely any action on it; while at the boiling point ammonia is disengaged, but the ebullition must be long continued to effect complete decomposition.

Anhydrous oxide of mercury and ammonia is much more fixed, as potassa decomposes it only when heated to the fusing point of the alkali. The combination exhibits all the characters of a powerful base: it combines with the acids and forms well-defined salts. It absorbs carbonic acid nearly as readily as lime and baryta, and its carbonate does not decompose at  $212^\circ$ ; it also expels ammonia from its salts as rapidly as lime and baryta. The proportion of oxide of mercury and ammonia represented by the formula  $3\text{HgO}, \text{HgNH}_2$ , corresponds to 1 equivalent of a base RO, and saturates 1 equivalent of acid.

The following compounds have, thus far, been obtained:

Hydrated base.....	$3\text{HgO}, \text{HgNH}_2 + 3\text{HO}$ .
Intermediate hydrate.....	$3\text{HgO}, \text{HgNH}_2 + \text{HO}$ .
Anhydrous base.....	$3\text{HgO}, \text{HgNH}_2$ .
Sulphate.....	$(3\text{HgO}, \text{HgNH}_2), \text{SO}_3$ .
Hydrated carbonate.....	$(3\text{HgO}, \text{HgNH}_2), \text{CO}_3 + \text{HO}$ .
Carbonate dried at $275^\circ$ .....	$(3\text{HgO}, \text{HgNH}_2), \text{CO}_3$ .
Oxalate.....	$(3\text{HgO}, \text{HgNH}_2), \text{C}_2\text{O}_3$ .
Nitrate.....	$(3\text{HgO}, \text{HgNH}_2), \text{NO}_5 + \text{HO}$ .
Bromate.....	$(3\text{HgO}, \text{HgNH}_2), \text{BrO}_5$ .

Several chlorides and iodides are also known which are derived from the oxide of mercury and ammonia by reactions resembling those by which the ordinary metallic oxides are converted into chlorides and iodides. The formulæ of these compounds are:

Chloride.....	$(2\text{HgO}, \text{HgCl}), \text{HgNH}_2$ .
Another chloride.....	$3\text{HgCl}, \text{HgNH}_2$ .
Iodide.....	$(2\text{HgO}, \text{HgIo}), \text{HgNH}_2$ .

*Sulphate of Mercury and Ammonia.*

§ 1097. If protosulphate of mercury  $\text{HgO}, \text{SO}_3$  be added, by small quantities at a time, to caustic ammonia, the salt is dissolved in very large quantity; but if the liquid be diluted with a great deal of water, a copious white precipitate forms, which was long known as *ammoniacal turpeth*, and which may be regarded as the sulphate of

mercury and ammonia ( $3\text{HgO}, \text{HgNH}_2\text{SO}_3$ ). The composition of this product does not, however, appear to be constant.

*Carbonate of Mercury and Ammonia.*

§ 1098. This salt is readily prepared by the direct combination of carbonic acid with oxide of mercury and ammonia suspended in water; when an insoluble yellow compound, consisting of the hydrated carbonate, is obtained. It parts with its water at about  $284^\circ$  and passes into the state of anhydrous carbonate.

*Oxalate of Mercury and Ammonia.*

§ 1099. The oxalate of mercury and ammonia is obtained by digesting the protoxalate of mercury, made by double decomposition, with caustic ammonia in excess, when a white granular powder is obtained, which explodes when heated.

COMPOUNDS OF MERCURY WITH SULPHUR.

§ 1100. If a current of sulphhydric acid be passed through a solution of a subsalt of mercury a black precipitate is obtained, which is the *sulphide of mercury*  $\text{Hg}_2\text{S}$ , corresponding to the suboxide  $\text{Hg}_2\text{O}$ ; but if the temperature be raised the precipitate is rapidly converted, even in the water, into the protosulphide  $\text{HgS}$ , and into metallic mercury.

If a current of sulphhydric acid be passed through a solution of a protosalt of mercury, there results first a white precipitate, which is a compound of protosulphide of mercury with the mercurial salt subjected to the reaction. Thus, the protosulphate  $\text{HgO}, \text{SO}_3$  is converted into a compound of which the formula is  $\text{HgO}, \text{SO}_3 + 2\text{HgS}$ , while the protonitrate  $\text{HgO}, \text{NO}_3$  gives the compound  $\text{HgO}, \text{NO}_3 + 2\text{HgS}$ , and the protochloride  $\text{HgCl}$  yields the product  $\text{HgCl} + 2\text{HgS}$ . But if the liquid be completely saturated by the gas, the precipitate turns black, and consists entirely of sulphide of mercury  $\text{HgS}$ , which, when heated in a retort, sublimes completely without change, and yields a red product of a crystalline fibrous texture, having the same composition as the black precipitate, and known by the name of *cinnabar*. The same compound is obtained by a continued trituration of mercury with sulphur, when a black substance is formed, which is sometimes used in medicine under the name of *æthiops mineral*. In order to obtain the sulphide of mercury  $\text{HgS}$ , it is better to rub together 6 parts of mercury and 1 of sulphur, the black substance which results yielding cinnabar by sublimation. Sulphide of mercury  $\text{HgS}$  is found in nature, most frequently in deep red, compact masses, but also forming, sometimes, beautiful red transparent crystals derived from the rhombohedron of  $71^\circ$ . It is the principal ore of mercury.

Under the ordinary pressure of the atmosphere, cinnabar volatilizes before fusing, and produces a brownish-yellow vapour, the

density of which is 5.4, while the specific gravity of solid cinnabar is 8.1.

The sulphide of mercury  $\text{HgS}$  sometimes exhibits a red colour more beautiful than that of sublimed cinnabar, and is used in oil and aquarelle painting under the name of vermilion. The most beautiful vermilion is prepared by the reaction, assisted by water, of the alkaline polysulphides on sulphide of mercury: 300 parts of mercury and 114 of sulphur being triturated for 2 or 3 hours in a mortar, and 75 parts of potassa and 400 of water added, the whole is maintained at a temperature of about  $113^\circ$ , and shaken from time to time, when the black precipitate soon turns red; and when it has attained the proper shade, it is rapidly washed with hot water. If the action of the alkaline sulphide were prolonged too much, the substance would again become brown. Very fine vermilion is also obtained by heating, for a considerable length of time, at an average temperature of  $122^\circ$ , ordinary cinnabar, reduced to an impalpable powder, with a solution of alkaline sulphide. The phenomenon of the change of colour of the sulphide of mercury, by contact with the alkaline sulphides, has not yet been properly explained.

Cinnabar is manufactured on a large scale in the furnaces for working ores of mercury. At Idria, in Carinthia, 100 parts of mercury and 18 parts of powdered sulphur are placed in small wooden tubs, which are turned for 3 or 4 hours around their horizontal axis, when a black sulphide of mercury is formed, which is then sublimed in cast-iron vessels, covered with capitals of baked clay, on which the cinnabar condenses.

Cinnabar is readily roasted in the air, sulphurous acid being disengaged, while metallic mercury distils over. It is easily decomposed by hydrogen, carbon, and many of the metals. The non-oxidizing acids act on it with difficulty, while it is readily attacked by concentrated nitric acid, and especially by aqua regia.

#### COMPOUNDS OF MERCURY WITH CHLORINE.

§ 1101. Two compounds of mercury with chlorine are known:

The subchloride  $\text{Hg}_2\text{Cl}$ , called *calomel*; and

The protochloride  $\text{HgCl}$ , commonly called *corrosive sublimate*.

The majority of chemists, even at this day, give the name of *protochloride of mercury* to calomel  $\text{Hg}_2\text{Cl}$ , and that of *bichloride* to corrosive sublimate  $\text{HgCl}$ ; but we have not retained these names, because they clash with the rules of nomenclature and chemical formulæ which it has been agreed to assign to these substances. We deem it necessary to insist particularly on this point, in order to avoid mistakes, which might prove very serious, because these substances are used in medicine.

The subchloride  $\text{Hg}_2\text{Cl}$  may be prepared by pouring a solution of subnitrate of mercury into a dilute solution of sea salt, the subchloride of mercury  $\text{Hg}_2\text{Cl}$  being precipitated in the form of a white

powder. It may be also obtained by the reaction of metallic mercury on protochloride of mercury  $\text{HgCl}$ , or corrosive sublimate, for which purpose 4 parts of corrosive sublimate and 3 parts of mercury are mixed and rubbed together for some time, moistening the whole with a small quantity of alcohol, to prevent injury from the poisonous dust of the sublimate. It is then heated in a large phial, in a sand-bath, when the calomel sublimes and condenses in the upper part of the phial. As this product may be mixed with corrosive sublimate, it is necessary to reduce it to a fine powder, and wash it with boiling water until the water affords no precipitate with potassa or sulfhydic acid. Calomel is prepared in manufactories of chemical products by heating a mixture of subsulphate of mercury  $\text{Hg}_2\text{O}, \text{SO}_3$  and sea salt; but as the preparation of the subsulphate is somewhat difficult, a mixture of protosulphate of mercury  $\text{HgO}, \text{SO}_3$  and metallic mercury is substituted. Sixteen parts of mercury being divided into two equal portions, the first is converted into protosulphate (§ 1092) and mixed intimately with the second portion, after which the mixture is rubbed up with 3 parts of sea salt and the whole distilled.

Calomel used in pharmacy should be very finely powdered, because it is then more easily separated from the corrosive sublimate, which acts as a poison on the animal economy. It is obtained immediately in an impalpable powder by effecting the distillation in a vessel, the wide and short neck of which enters a large receiver, where the calomel vapour condenses before touching its sides. The calomel thus obtained should be washed with boiling water until no precipitate is formed by potassa or sulfhydic acid.

By subliming large quantities of calomel, beautiful transparent crystals are frequently obtained, which are square prisms, having an octohedral termination. They are remarkable for their great refracting and dispersive power, and belong to the second system of crystallization. Light slowly decomposes subchloride of mercury, and causes it to assume a grayish hue, owing to the disengagement of chlorine, while a portion of the mercury is set free. The density of this substance is 6.5; and it fuses and volatilizes at nearly the same temperature under the ordinary pressure of the atmosphere. The density of its vapour is 8.2, the gaseous chloride being therefore composed of

1 vol. vapour of mercury.....	6.976
$\frac{1}{2}$ " chlorine .....	1.220
1 vol. gaseous subchloride $\text{Hg}_2\text{Cl}$ .....	8.196

Calomel is very slightly soluble in water, and a solution of 1 part of chlorohydric acid in 250,000 parts of water is very sensibly affected by subnitrate of mercury. In time, chlorohydric acid acts on it at the boiling point, when metallic mercury separates, while the protochloride  $\text{HgCl}$  is dissolved. Concentrated nitric acid soon



converts it into corrosive sublimate and protonitrate of mercury. Aqua regia and a solution of chlorine dissolve it in the state of protochloride  $\text{HgCl}$ . Calomel combines readily with dry ammoniacal gas, producing a black compound, of which the formula is  $\text{Hg}_2\text{Cl} + \text{NH}_3$ , and which, when treated with liquid ammonia, yields a gray powder of the formula  $\text{Hg}_2\text{Cl}, \text{HgNH}_2$ .

Calomel is used in medicine as a vermifuge and purgative, and is also applied to the treatment of venereal diseases.

*Protochloride of Mercury  $\text{HgCl}$ , or Corrosive Sublimate.*

§ 1102. Corrosive sublimate can be prepared by dissolving mercury in aqua regia containing an excess of chlorohydric acid, when, by treatment with boiling water, the greater part of the protochloride is deposited in acicular crystals during the cooling of the liquid. This compound is generally prepared on a large scale, by heating on a sand-bath a mixture of protosulphate of mercury  $\text{HgO}, \text{SO}_3$  and sea salt, when the protochloride sublimes on the upper parts of the distilling apparatus. The protosulphate of mercury often contains a small quantity of subsulphate, which yields calomel by its reaction on sea salt; to avoid which, a small quantity of peroxide of manganese is generally added to the mixture. As corrosive sublimate fuses at a pressure much below that at which it distils at the ordinary pressure of the atmosphere, advantage is taken of this property to give more consistency to the sublimed product; to effect which, the fire is increased toward the close of the operation, when the sublimate, by beginning to fuse, is more compactly aggregated. When the distilling vessels are cool they are broken, and the cakes of corrosive sublimate removed.

Protochloride of mercury is colourless, and its density is 6.5. It fuses at about  $509^\circ$ , and boils at about  $563^\circ$  under the ordinary pressure of the atmosphere, yielding a colourless vapour, the density of which is 9.42. Gaseous protochloride therefore contains

1 vol. vapour of mercury.....	6.976
1 “ chlorine.....	2.440
1 vol. gaseous chloride $\text{HgCl}$ .....	9.416

Corrosive sublimate dissolves in 16 parts of cold and 3 parts of boiling water, and its curve of solubility is represented on the plate at page 407, vol. i. It is more easily soluble in alcohol than in water, as  $2\frac{1}{3}$  of absolute and  $1\frac{1}{2}$  of boiling alcohol dissolve 1 part of the binary compound. It is also soluble in 3 parts of cold ether.

It dissolves readily in a solution of chlorohydric acid, especially when the latter is hot, and the liquid sets in a crystalline mass on cooling.

Corrosive sublimate is often used in the laboratory as an agent of chlorination; and it has already been shown (§ 943) that bichloride of tin is obtained by distilling a mixture of 1 part of tin

filings and 5 parts of sublimate. Many substances also abstract from it, by the humid way, a portion of its chlorine, and cause it to pass into the state of subchloride, which decompositions are more easily effected when assisted by solar light.

Corrosive sublimate is sometimes employed in medicine, chiefly in the treatment of venereal diseases; but, being a dangerous medicine, it should only be administered with the greatest care. It is used advantageously to protect wood from insects, and wooden bedsteads may be kept free from vermin by impregnating the wood with a weak solution of sublimate. Zoological specimens and anatomical preparations are frequently preserved by being soaked in a dilute solution of it.\*

Protochloride of mercury forms, with the metallic chlorides, a great number of crystallizable double chlorides. Three of these compounds with chloride of potassium have been obtained, the formulæ of which are  $\text{KCl} + \text{HgCl} + \text{HO}$ ,  $\text{KCl} + 2\text{HgCl} + 2\text{HO}$  and  $\text{KCl} + 4\text{HgCl} + 4\text{HO}$ . But one compound has been obtained with chlorohydrate of ammonia, with the formula  $\text{NH}_3, \text{HCl} + \text{HgCl} + \text{HO}$ , and isomorphous with the corresponding compound with chloride of potassium.

When caustic alkalies or alkaline carbonates are poured into a solution of corrosive sublimate, very variable compounds are obtained, according to the proportions of the reacting substances and the temperature and degree of concentration of the liquids. When the alkali is in excess the yellow or red oxide is produced; but by using the reagent in weaker and more varying proportions, gray, red, or violaceous precipitates are obtained, which are oxychlorides; the formulæ are  $2\text{HgO}, \text{HgCl}$ ,  $3\text{HgO}, \text{HgCl}$ ,  $4\text{HgO}, \text{HgCl}$ . Analogous oxychlorides are obtained by boiling oxide of mercury with a solution of corrosive sublimate.

Ammonia, poured into a solution of corrosive sublimate, throws down white precipitates, making the liquid emulsive and varying in composition. They have all, for a long time, been indiscriminately called *white precipitate*, but are now divided into several well-defined compounds. If a solution of corrosive sublimate be poured into a solution of caustic ammonia, and the precipitate be washed with cold water, a white substance is obtained, of which the formula is  $\text{Hg}_2\text{ClNH}_2$ , and which is called *chloramide of mercury*, because it is admitted to contain the compound  $\text{NH}_2$ , which is called *amide*, (§ 514.) The reaction from which this product arises is represented by the following equation:




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\* Meat may be kept fresh for a great length of time, by being allowed to remain for several hours in a bucket filled with water into which the merest trace of corrosive sublimate has been thrown; and several other metallic salts, especially nitrate of silver, have the same property. This method of preserving meat would, however, be too dangerous for family use.—*W. L. F.*

The formula  $\text{HgCl}, \text{HgNH}_2$  is sometimes assigned to this substance. It is decomposed by boiling water, and, when heated, gives off ammonia, ammoniacal chloride of mercury  $2\text{Hg}_2\text{Cl}, \text{NH}_3$ , and leaves in the retort a red compound, which is destroyed only at a temperature of  $662^\circ$ , and of which the composition is represented by the formula  $2\text{HgCl} + \text{NHg}$ .

By boiling chloramide of mercury with water until the substance no longer undergoes any change, a white compound of which the formula is  $(2\text{HgO}, \text{HCl})\text{HgNH}_2$  is obtained, which may be regarded as the chloride of the compound oxide of mercury and ammonia  $3\text{HgO}, \text{HgNH}_2$ ; and, in fact, when treated with potassa, it is converted into oxide of mercury and ammonia.

If caustic ammonia be dropped into a solution of corrosive sublimate, taking care to keep the latter substance always in excess, a white precipitate is obtained, of which the formula may be written  $3\text{HgCl}, \text{HgNH}_2$ , and which is then regarded as oxide of mercury and ammonia, in which all the oxygen is replaced by an equivalent quantity of chlorine. This compound is soon changed even by washing in cold water.

#### COMPOUNDS OF MERCURY WITH BROMINE.

§ 1103. Mercury forms with bromine two compounds which correspond to the two chlorides. The bromide  $\text{Hg}_2\text{Br}$  is obtained by pouring a solution of bromide of potassium into that of subnitrate of mercury, when the precipitate which forms is nearly insoluble in water, and volatilizes without change. The bromide of mercury  $\text{HgBr}$  is obtained by pouring bromine in excess on mercury covered by a stratum of water, when the mercury soon dissolves in the state of protobromide, which may be crystallized by evaporation. The protobromide may then be sublimed without alteration, and it forms crystallizable compounds with the alkaline bromides.

#### COMPOUNDS OF MERCURY WITH IODINE.

§ 1104. By adding iodide of potassium to a solution of corrosive sublimate, a red precipitate of protiodide of mercury  $\text{HgI}$  is obtained, which may also be prepared by triturating together equal quantities of mercury and iodine, with a small quantity of alcohol to assist their reaction. The protiodide of mercury dissolves largely in a hot solution of iodide of potassium, and the liquid, on cooling, deposits a portion of the protiodide in the form of beautiful red crystals. If the red iodide of mercury be heated, it suddenly changes colour and becomes of a clear yellow, while, if the temperature be raised still higher, it fuses into a yellow liquid, and sublimes in the form of yellow crystals. The fused yellow iodide and the large yellow crystals frequently retain their colour, even after cooling; but the substance, on being broken, turns red, first at the

point of the rupture, and then gradually through the whole mass, which change of colour is very rapid when the substance is powdered. The protiodide of mercury presents, therefore, two modifications, distinguishable by their colour, and which also affect two different crystalline forms, the primitive form of the red crystals being an octahedron with a square base belonging to the second system, while the yellow crystals belong to the fourth.

Protiodide of mercury volatilizes without change, and the density of its vapour has been found to be 15.68, being the greatest of all gaseous bodies. It is very slightly soluble in water, only in the proportion of 1 to 150.

An iodide of mercury  $\text{Hg}_2\text{I}$  is obtained by pouring iodide of potassium into a solution of subnitrate of mercury, as a dirty-green precipitate, which volatilizes unchanged when rapidly heated, and which, on the contrary, is decomposed into protiodide of mercury  $\text{HgI}$  and metallic mercury when heated slowly.

#### COMPOUND OF MERCURY WITH CYANOGEN.

§ 1105. Only one compound of mercury with cyanogen is known, corresponding to the protoxide  $\text{HgO}$ . The combination is made by dissolving protoxide of mercury in cyanohydric acid, for which purpose the dilute cyanohydric acid obtained by the solution of the ferrocyanide of potassium in dilute sulphuric acid is used. Cyanide of mercury is generally prepared in the laboratory by boiling together 8 parts of Prussian blue, 1 of protoxide of mercury, and 8 of water, when the boiling solution, after being filtered, deposits on cooling white prismatic crystals of anhydrous cyanide of mercury  $\text{HgCy}$  or  $\text{HgC}_2\text{N}$ . When, as often happens, the liquid contains a small quantity of iron in solution, it is boiled with protoxide of mercury, which precipitates the oxide of iron. Cyanide of mercury may also be prepared by boiling 2 parts of ferrocyanide of potassium with 3 of protosulphate of mercury dissolved in 15 or 20 parts of water; when the liquid deposits, on cooling, crystals of cyanide of mercury.

The affinity of mercury for cyanogen is considerable, as oxide of mercury decomposes cyanide of potassium, potassa and cyanide of mercury being formed. When boiled for a long time the protoxide of mercury dissolves in the cyanide of mercury, and the liquid deposits crystals of oxycyanide of mercury. Cyanide of mercury combines with a great number of metallic cyanides, and yields crystallizable double cyanides. The double cyanide of mercury and potassium crystallizes in regular octahedrons of the formula  $\text{KC}_2\text{Cy} + \text{HgCy}$ . Cyanide of mercury also combines with the chlorides, alkaline bromides, and iodides, forming several crystallizable compounds.

## COMPOUND OF MERCURY WITH NITROGEN.

§ 1106. If dry ammoniacal gas be passed over protoxide of mercury, prepared by the humid way, until the latter can absorb no more, and the product be then slowly heated in an oil-bath to  $302^{\circ}$ , still maintaining the current of ammonia, a brown powder is obtained, which is a compound of mercury with nitrogen, having the formula  $Hg_3N$ . The substance is generally mixed with a small quantity of suboxide of mercury, which can be removed by weak nitric acid. Nitride of mercury detonates by heat, and by percussion, or by contact with concentrated sulphuric acid properly prepared. Acids dissolve it, producing mixtures of mercurial and ammoniacal salts.

## DETERMINATION OF MERCURY, AND ITS SEPARATION FROM THE METALS PREVIOUSLY DESCRIBED.

§ 1107. Mercury is generally determined in the metallic state, and sometimes also in the state of subchloride  $Hg_2Cl$ . In order to separate mercury from its compounds, under conditions in which the metal can be very exactly weighed, a tube *ab* of hard glass is employed, resembling those used in the analysis of organic substances, and drawn out in one of its ends, as represented in fig. 578,



Fig. 578.

having a globe A at the narrow portion, in which the mercury condenses. A small quantity of asbestos being placed at *a* in the tube, upon it is poured a volume of quicklime, and the mercurial substance, exactly weighed, is introduced at *c*, and lastly, the tube is filled with lime. This being done, the tube is arranged over a sheet-iron furnace, and a current of dry hydrogen gas passed through the extremity *b*; the anterior portion *ca* of the tube containing the lime being first heated, while the coals are gradually carried toward the end *b*. The mercurial product is decomposed, the mercury is carried over in the state of vapour by the hydrogen gas and condenses in the globe A, while the small quantity of water which sometimes also collects there is soon carried off by the dry hydrogen. At the close of the operation, the globe A is detached and weighed with the mercury it contains; after which the metal is poured out, and, for greater exactness, the interior of the globe is washed with nitric acid and then with distilled water. The globe, being empty and perfectly dry, is weighed, and the weight of the condensed mercury thus ascertained. In order to obtain exact results, care must be had that the temperature of the globe does not rise, in consequence of the condensation of a large quantity of water, as in that case a small quantity of vapour of mercury would be lost.

When the mercurial product contains nitric acid metallic copper must be substituted for the lime, in order to decompose the nitrous vapours, which would attack the mercury in the globe A.

§ 1108. Advantage is generally taken of the volatility of mercury to separate it from the other metals with which it is mixed. When it is dissolved in acids it is always precipitated by sulphydric acid, and the precipitate is then restored to the metallic state by heating the product, mixed with a small quantity of quicklime, in a current of hydrogen gas. When the sulphide of mercury is mixed with other metallic sulphides the latter are separated, as the mercury alone distils over.

When the mercury is precipitated from its solutions in the metallic state by a blade of iron, or by protochloride of tin, it is still necessary, in order to obtain it perfectly pure, to distil it in the apparatus first described.

#### ALLOYS OF MERCURY, OR AMALGAMS.

§ 1109. Mercury combines with a large number of metals, forming alloys, called *amalgams*, which are fluid when the mercury largely predominates, and solid in the contrary case. The presence of a very small quantity of foreign metal suffices to destroy the fluidity of mercury and its other physical characters.

Mercury combines with potassium and sodium and evolves heat, while doughy amalgams are formed which decompose water. With lead and tin it forms amalgams the consistency of which varies with the proportion of metal combined. If these amalgams be heated so as to make them perfectly liquid, and then allowed to cool slowly, crystals of solid amalgam separate, exhibiting compounds of definite proportions. An amalgam of silver, crystallized in regular dodecahedrons, and the usual composition of which is expressed by the formula  $Hg_2Ag$ , is found in nature. Amalgams are readily decomposed by heat, and give off the whole of their mercury, which distils over.

#### PLATING OF MIRRORS.

§ 1110. Mirrors are made by covering one side of the glass with an amalgam of mercury and tin in the following manner:—A sheet of tin-foil, of the same size as the glass, is laid upon a very smooth marble table, set in a wooden frame and surrounded by little canals. The table, which is movable and may be inclined in various ways, is first made perfectly horizontal, and the sheet of tin, being smoothed with a hare's foot, is then completely saturated with mercury applied by the same instrument. It is then covered with a coat of mercury 4 or 5 millimetres in thickness, after which the glass plate is brought to the end of the table, and pushed over the sheet of tin, so as to drive before it the mercury in excess, which runs into the canal around the table. The glass is then loaded with lumps of plaster, distributed uniformly over its surface, and the table is inclined to facilitate the escape of the mercury expelled by pressure. It is then left in this position for 15 or 20 days, after which the

coating adhering to the glass is composed of about 4 parts of tin and 1 of mercury.

#### METALLURGY OF MERCURY.

§ 1111. The principal ore of mercury is the sulphide or cinnabar, which mineral is found in two different geological positions. It sometimes forms veins in the oldest transition rocks, and sometimes is scattered through the strata of sandstone, schist, or compact limestone, which appear to belong to the Jurassic epoch. The famous mines of Almaden, in the province of La Mancha in Spain, consist of veins traversing micaceous transition schists, while the mines of Idria, in Illyria, are an example of the second formation. Mercury is also found in the native state, in small globules scattered through bituminous strata, but always in the vicinity of bearings of cinnabar, and probably arising from certain chemical reactions which have taken place in the bosom of the earth.

Mercury is procured from cinnabar, at Idria and Almaden, by roasting the ore in a distilling apparatus, when the sulphur burns in the state of sulphurous gas, while the mercury, being set free, distils over and condenses in the chambers.

§ 1112. Figures 579, 580, and 581 represent the apparatus used at Idria. A is a large roasting furnace (figs. 579 and 581) furnished on each side with a series of condensing chambers C, C,...D. The ore in large pieces is heated on an arch *nn'* having a great num-

Fig. 579.

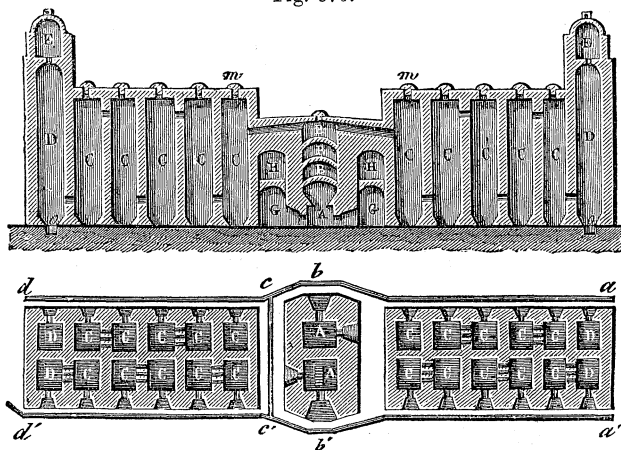


Fig. 580.

ber of holes, until the space *V* is entirely filled with it, while on the second arch *pp'* smaller pieces of ore are placed; and lastly, on a third *rr'*, the dust and mercurial residues of preceeding operations are changed. The pulverulent ore is placed in earthen vessels with

which the space U is entirely filled; and when the furnace is charged, fire is kindled on the grate F, and the temperature is gradually raised. The sulphide of mercury roasts in a very oxidizing current of air, which enters the furnace by small canals opening

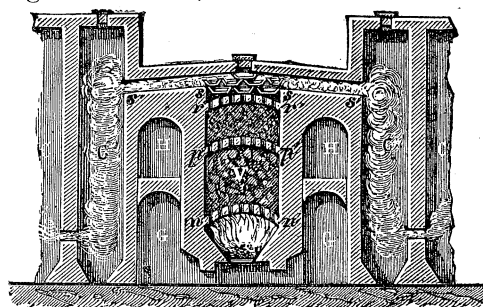


Fig. 581.

into the spaces G, H, and the mercurial vapours are carried into the condensing chambers C, C, C, C, in the first three of which the greater portion of the metal condenses, whence it flows into the conduits *abcd, a'b'c'd'*, which convey it into a reservoir. A great deal of water and but little mer-

cury condenses in the last chamber; and as the latter is mixed with dust, it is collected in separate conduits, and then purified by filtering, while the residue is again introduced into the furnace. In order to condense the last mercurial vapours in the last chambers E, D, water is poured over the inclined planes which extend from one side to the other, and between which the gas and vapours are obliged to circulate before passing out into the atmosphere.

The mercury is filtered through ticking-cloth, and then placed in cast-iron bottles, each containing about 60 pounds.

The ore at Idria consists of several kinds, according to the nature of the substances with which the cinnabar is intimately mixed. The richest ores, which are found in limestone, and yield 50 to 60 per cent. of mercury, are called *stahlerz*; and the *lebererz*, or cinnabar scattered through very bituminous schist yields 40 to 50 per cent. of mercury. The *ziegelerz* only contain from 10 to 20 per cent., as in them the sulphide is disseminated in schists and quartzose sandstone.

§ 1113. Certain parts of the veins at Almaden contain pure cinnabar, while the greater portion is composed of cinnabar scattered through quartzose and argillaceous gangues, yielding only about 10 per cent. of mercury. The Spanish mines furnish annually more than 2000 tons of mercury.

At Almaden, as at Idria, the treatment consists in roasting the ore in furnaces, one of which is represented in figs. 582 and 583, and which, in Spain, are called *buytrones*. The furnace consists of a prismatic space AB, separated into two compartments by a brick arch pierced with holes. The ore is heaped in the space B above the arch, the larger pieces being at the bottom, and the whole is covered with bricks made of a mixture of clay, powdered ore, and mercurial dust arising from the operation. At the upper part of



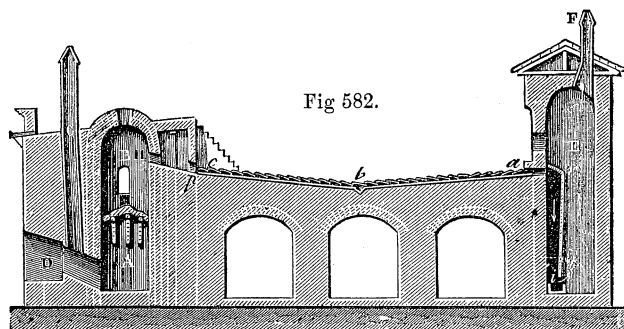


Fig. 582.

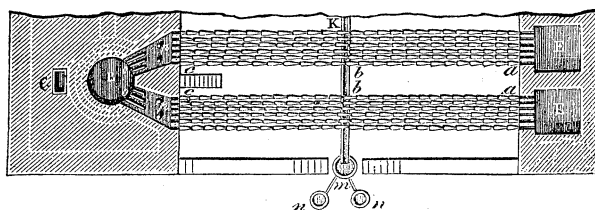


Fig. 583.



Fig. 584.

the furnace B, apertures *p* communicate with earthen receivers, arranged on each other in rows. Fig. 584 represents some of these receivers or *aludells*. The condensed mercury oozes through the joints of the aludells on the lower row, and flows into a canal *bb*, which conveys it into a receiving basin *m, n, n*, while the gases, mixed with the mercurial vapours which have not been condensed, are conveyed into a chamber E, where mercurial dust, which is to be removed from time to time, is deposited. The dust yields, by filtering, a certain quantity of fluid mercury, and the

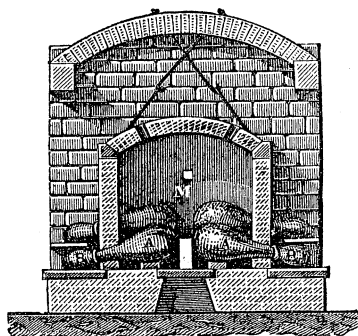


Fig. 585.

residue is mixed with clay of which clay bricks are made, to be again heated in the furnace as above stated. The firing lasts for 12 or 13 hours, after which the furnace is allowed to cool for 3 or 4 days, when the materials are withdrawn and a second operation commenced.

§ 1114. Mercurial ores, consisting of mixtures of cinnabar and limestone, are also found in the duchy of Deux-Ponts, (France,) and are worked by being heated in earthen retorts A (fig. 585) furnished with

earthen receivers B, and disposed in a galley-furnace M. A certain quantity of water is placed in the receivers, where the sulphide of mercury in this case is decomposed by the lime, while sulphide of calcium and sulphate of lime are found. The mercury set free condenses in the receivers.

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## SILVER.

EQUIVALENT = 108 (1350.0; O = 100).

§ 1115. The silver used for coin and plate is never pure, but contains a certain proportion of copper. In order to obtain pure silver the alloyed metal is dissolved in nitric acid and sea-salt added to the solution, when the silver is precipitated in the state of insoluble chloride, while the other metals remain in solution. 100 parts of the dried chloride of silver being mixed up with 70 of chalk and 4 or 5 of charcoal, are introduced into a clay crucible and heated to a strong, white-heat, when carbonic oxide is disengaged, while chloride of calcium and metallic silver are formed. After cooling, the silver is found in a button, at the bottom of the crucible, covered by a slag of chloride of calcium.

Silver is distinguished from all other metals by its brilliant white colour, and a lustre which does not tarnish in the air, unless the latter contain sulphuretted vapours. When highly polished, silver reflects light and heat better than any other metal, and its radiating power is, consequently, very feeble, for which reason a close silver vessel will retain the heat of a liquid which it may contain longer than a vessel of any other metal. Silver, the density of which of 10.5, is harder than gold, but softer than copper, while the addition of a small quantity of copper increases its hardness. It is the most malleable of the metals, after gold, and can be beaten into very thin leaves, and drawn out into extremely fine wire. It possesses also great tenacity, for a wire of 2 millimetres in diameter breaks only under a weight of 85 kilogrammes.

The fusing point of silver, which is at a white-heat, is supposed to be about 1000° of the air thermometer. It gives off very appreciable vapours at the temperature of a forge-fire, and soon volatilizes when exposed to the elevated temperature obtained between two coals terminating the conductors of a powerful battery.

Silver may be crystallized in cubes by fusion by the method stated, (§ 991), and native silver, which is often found in beautiful crystals, also affects the cubic form, modified by the faces of the octahedron or other simple forms of the regular system. The small

crystals obtained by precipitating silver by means of feeble galvanic action are likewise cubes.

Although silver neither absorbs oxygen at the ordinary temperature, nor combines permanently with that substance at a high temperature, it will, when kept in a very pure state for a long time fused in the air, absorb a considerable proportion of oxygen, with which it parts, on cooling, before solidifying. A portion of the metal is frequently thrown out of the crucible by the evolution of the gas. The absorbing power of silver is shown by the following experiment:—3 or 4 kilogrammes of very pure silver are fused in an earthen crucible, and when the metal has attained a very high temperature the crucible is uncovered, and a small quantity of saltpetre is added, which, by decomposing, maintains an atmosphere of oxygen in the crucible. After the addition of the last portion of the saltpetre the crucible is kept covered for half an hour, the high temperature still being maintained, and is then plunged into a water-cistern, beneath a bell-glass filled with water, when the oxygen absorbed is immediately disengaged, and collected in the glass.

It has been ascertained that silver can absorb 22 times its volume of oxygen, which property is destroyed by the presence of a very small quantity of foreign metals.

Silver is not oxidized, at a red-heat, by contact with the caustic alkalies and alkaline nitrates, for which reason silver crucibles are used when, in chemical analysis, substances are to be treated with caustic potassa or saltpetre, which would attack platinum crucibles. But silver is affected by fused alkaline silicates, oxide of silver, which dissolves in the silicate and colours it yellow, being formed.

Silver decomposes, only in a very feeble manner, chlorohydric acid in solution, and reaction takes place only when the metal is very finely divided and the acid is kept at the boiling point. Dilute sulphuric acid does not attack silver, while the acid when hot and concentrated soon decomposes it, sulphurous acid being disengaged while sulphate of silver is formed. Nitric acid acts on silver, even at the ordinary temperature, disengaging deutoxide of nitrogen and converting the silver into a nitrate. Sulfhydric acid is decomposed by silver at the ordinary temperature; and a polished blade of silver soon blackens in a solution of a sulfhydric acid, and becomes covered with a black pellicle of sulphide of silver. Chlorine, bromine, and iodine act on silver even when cold.

#### COMPOUNDS OF SILVER WITH OXYGEN.

§ 1116. Three compounds of silver with oxygen are known:

The suboxide,  $\text{Ag}_2\text{O}$ .

The protoxide,  $\text{AgO}$ .

The binoxide,  $\text{AgO}_2$ .

The protoxide is the only oxide of silver possessing any interest.

By heating to  $212^{\circ}$  in a current of hydrogen gas, certain salts formed by the protoxide of silver with organic acids, for example the nitrate, the protoxide loses one-half of its oxygen, and a subsalt of silver is formed, which dissolves in water and produces a brown solution, from which caustic potassa precipitates the suboxide  $\text{Ag}_2\text{O}$  as a black powder. The subsalts of silver appear to be formed under several other circumstances, when protosalts of the metal are subjected to deoxidizing agencies.

*Protoxide of silver*  $\text{AgO}$  is obtained by pouring potassa in excess into a solution of nitrate of silver, when a brown precipitate of hydrated protoxide is formed, which readily parts with its water in a dry vacuum or at a moderate heat, becoming converted into an olive-coloured powder of anhydrous protoxide. Heat soon drives off the oxygen from the protoxide of silver, and it is also decomposed by the solar rays. The hydrated protoxide dissolves slightly in water and causes the latter subsequently to exert an alkaline reaction on coloured tinctures; but it does not combine with the caustic alkalies. Protoxide of silver is a powerful base which combines with even the most feeble, and completely neutralizes the most powerful acids; thus nitrate of silver behaves perfectly neutral with coloured litmus paper.

When the two platinum conductors of a battery are dipped into a dilute solution of nitrate of silver, contained in a W shaped tube, the positive conductor becomes coated with brilliant, black prismatic crystals of *binocide of silver*  $\text{Ag}_2\text{O}$ , which is more fixed than the protoxide, as it resists a temperature of  $212^{\circ}$  and is decomposed only at about  $302^{\circ}$ , when it is converted immediately into metallic silver. It disengages oxygen when in contact with acids, yielding protosalts of silver. With chlorohydric acid it evolves chlorine. It decomposes ammonia with effervescence, the oxygen given off by the binocide while the latter is reduced to protoxide, uniting to form water with the hydrogen of the ammonia, while nitrogen is disengaged.

#### *Ammoniuret of Oxide of Silver.*

§ 1117. By digesting oxide of silver with a concentrated solution of caustic ammonia, a black, highly explosive powder is formed, which is also obtained by pouring caustic potassa into the solution of a salt of silver in an excess of caustic ammonia. This compound, called *fulminating silver*, detonates very easily, and should be handled with the greatest care, as it even explodes under water when the latter is heated to  $212^{\circ}$ . Chemists are not agreed as to the composition of fulminating silver; while some regard it as formed by the direct combination of ammonia with oxide of silver, and assign it the formula  $\text{AgO}, \text{NH}_3$ , others consider it as an amide of silver  $\text{AgNH}_2$  produced by the reaction  $\text{AgO} + \text{NH}_3 = \text{AgNH}_2 + \text{HO}$ ; and lastly, a large number suppose it to be a simple nitrate of silver arising from the reaction expressed by the equation  $3\text{AgO} + \text{NH}_3 = \text{Ag}_3\text{N} + 3\text{HO}$ .

## SALTS FORMED BY PROTOXIDE OF SILVER.

§ 1118. As has already been said, (§ 1116,) protoxide of silver is a powerful base, which combines with even the weakest acids, and perfectly neutralizes powerful acids as regards their action on coloured reagents. Under some circumstances potoxide of silver even behaves like a base stronger than the alkalies, for it decomposes some alkaline salts by abstracting a portion of their acid; which reaction, however, only takes place when a double salt can be formed. The salts of silver are colourless when the acid itself is colourless. The soluble salts of silver are obtained by dissolving the carbonate of silver in acids, while those that are insoluble are prepared by double decomposition by means of the nitrate of silver obtained by dissolving the metal in nitric acid. The soluble salts of silver have a disagreeable metallic taste, and are very poisonous. All the salts of silver are blackened by solar light: they are decomposed, and metallic silver separates. The soluble salts present the following characteristic reactions:

Potassa and soda throw down a brown precipitate of hydrated protoxide, which does not dissolve in an excess of reagent, while ammonia produces the same precipitate in neutral solutions, but redissolves it entirely when present in excess; and if the solution contains a great excess of acid, it is not clouded by ammonia, because a double salt of silver and ammonia, indecomposable by an excess of ammonia is formed. Carbonates of potassa and soda yield a dirty-white precipitate of carbonate of silver, which does not dissolve in an excess of reagent, and carbonate of ammonia produces the same precipitate, which dissolves in an excess of carbonate of ammonia and in caustic ammonia. The precipitated oxide and carbonate of silver are easily decomposed by heat, and yield a spongy mass of metallic silver, which becomes compact by percussion and presents all the physical characters of malleable silver.

Sulphydric acid produces a black precipitate of sulphide of silver, and the alkaline sulphydrates yield the same black precipitate, which does not dissolve in an excess of sulphydrate.

Ferrocyanide of potassium yields a white, and the cyanoferride or red prussiate, a brownish-red precipitate.

Chlorohydric acid and the soluble chlorides form in solutions of silver a white precipitate, which readily collects, on shaking, into a consolidated mass if the liquid contains an excess of nitric acid. This precipitate is insoluble in an excess of nitric acid, but dissolves readily in ammonia; and if the latter be saturated by an acid the chloride of silver is again precipitated. The precipitate soon turns black in the light, first assuming a violaceous hue, which distinguishes it from freshly precipitated subchloride of mercury  $\text{Hg}_2\text{Cl}$ , which is formed when a soluble chloride is poured into a solution of a subsalt of mercury, and which remains white for a long time. A blade of

zinc or iron brought into contact with the moist chloride decomposes it and separates the metallic silver.

The soluble iodides form, in solutions of silver, a yellowish-white precipitate of iodide of silver, which dissolves with difficulty in a great excess of acid or ammonia.

Silver is precipitated from its solutions in the metallic state by a great number of metals, particularly by iron, zinc, and copper. Mercury effects the same decomposition, but the silver precipitated combines gradually with the mercury until a solid amalgam is formed, the silver subsequently deposited forming long brilliant needles of an amalgam of silver, filling sometimes the whole solution. This crystallization is called the *arbor Dianæ*.

#### *Nitrate of Silver.*

§ 1119. Silver dissolves readily in nitric acid, and on evaporating the liquid the nitrate of silver formed crystallizes, in the anhydrous state, in the form of large colourless plates. Nitrate of silver is generally made, in the laboratory, from coin which contains  $\frac{1}{10}$  of its weight of copper, by dissolving it in nitric acid, and evaporating to dryness the blue solution obtained, which contains both nitrate of silver and nitrate of copper. The residue is fused in a porcelain capsule, at a temperature below a dull-red heat, when the nitrate of copper is converted into protoxide of copper  $\text{CuO}$ , which colours the fused nitrate of silver black. The temperature is maintained until the nitrate of copper is entirely decomposed, which is ascertained by extracting a certain portion by means of a glass rod, dissolving it in a small quantity of water, and pouring an excess of ammonia into the filtered solution; if the liquid does not turn blue the nitrate of copper is entirely decomposed. The substance is then dissolved in water, and the oxide of copper separated by filtration.

The oxide of copper remaining in the liquid may also be precipitated by oxide of silver. After having evaporated to dryness the solution of the nitrates to drive off the excess of acid, and dissolved the residue in water, about  $\frac{1}{5}$  of the liquid is separated, and is completely precipitated by caustic potassa in excess, when the oxides of silver and copper are deposited. They are washed with cold water and then boiled with the remaining  $\frac{4}{5}$  of the liquid, when the oxide of silver completely precipitates the oxide of copper, while nitrate of silver alone remains in solution, the deposit consisting of a large quantity of oxide of copper and very little oxide of silver.

Nitrate of silver is also frequently prepared from the chloride, which is always obtained in large quantities in laboratories where minerals are analyzed. The chloride of silver may be decomposed by lime, in a crucible heated to a white-heat, as stated, (§ 1115), and pure metallic silver may be thus obtained and afterwards dissolved in nitric acid; but generally, an iron rod, previously moist-

ened with water acidulated by chlorohydric acid, is dipped into the chloride of silver, which is thus gradually decomposed and, after some time, leaves only metallic silver, which is washed with acidulated water and dissolved in nitric acid.

Nitrate of silver is soluble in its weight of cold, and one-half of its weight of boiling water, and also dissolves in 4 parts of boiling alcohol. It has been mentioned that nitrate of silver fuses without change at a temperature below a dull-red: it solidifies on cooling into a crystalline mass, and, if further heated, it decomposes. At the commencement of the decomposition oxygen alone is disengaged, and the salt is transformed in the *nitrite*  $\text{AgO}, \text{NO}_2$ , while subsequently, both oxygen and nitrogen are disengaged, and finally metallic silver alone remains.

Fused nitrate of silver is used in surgery as a cauter, under the name of *lapis infernalis*, which is usually employed in the shape of small sticks fixed in the end of a pencil-holder. The sticks are made by pouring fused nitrate of silver into an iron mould similar to that represented in fig. 323, (page 445, vol. i.;) and because the sides of the mould decompose a small quantity of the nitrate, the sticks generally appear black at the surfaces.

Nitrate of silver is also used internally in certain forms of epilepsy, but it is a dangerous remedy and should be administered with great prudence. Persons who have taken this medicine should avoid exposure to the light of day until the salt of silver, which is distributed throughout the whole organism, has been carried off, without which precaution all the parts of the body exposed to light turn blue, in consequence of the decomposition of the salt of silver in the subcutaneous tissue.

Nitrate of silver is decomposed feebly by solar light, and more rapidly in the presence of organic substances. A drop of a solution of nitrate produces a brownish-black mark on the skin, which can be removed only by a solution of cyanide of potassium. When a piece of linen soaked in nitrate of silver is exposed to a current of hydrogen gas, it remains covered with metallic silver presenting a certain degree of lustre; which property has been applied to the silvering of designs on muslins, but without much success.

Nitrate of silver absorbs dry ammoniacal gas, and forms a compound of the formula  $\text{AgO}, \text{NO}_2 + 3\text{NH}_3$ , from which heat completely expels the ammonia. If nitrate of silver be poured into an excess of ammonia and the liquid be evaporated, it deposits crystals of which the formula is  $\text{AgO}, \text{NO}_2 + 2\text{NH}_3$ .

When a solution of nitrate of silver is boiled with very finely divided metallic silver, obtained by chemical preparation, a considerable quantity of silver will be found to dissolve; and compounds, analogous to those formed when a solution of nitrate of lead is boiled with metallic lead, (§ 967,) are probably produced.

*Sulphate of Silver.*

§ 1120. Sulphate of silver is obtained by heating metallic silver with concentrated sulphuric acid, when sulphurous acid is disengaged while a white crystalline powder of sulphate of silver is formed. It is also obtained by pouring sulphuric acid or sulphate of soda into a boiling solution of nitrate of silver, in which case the sulphate of silver is precipitated in the form of small prismatic crystals. During the cooling of the liquid, new crystals are deposited which are sufficiently developed to allow their shape, which is the same as that of anhydrous sulphate of soda, to be distinguished. Sulphate of silver is very slightly soluble in water, as hot water scarcely dissolves  $\frac{1}{100}$  part of it; but it readily dissolves in ammonia, and the liquid, when evaporated, yields crystals of a compound sulphate of silver and ammonia of the formula  $\text{AgO}, \text{SO}_3 + 2\text{NH}_3$ .

*Hyposulphite of Silver.*

§ 1121. Protoxide of silver has so great an affinity for hyposulphurous acid that it abstracts it from potassa and soda. If oxide of silver be digested with a solution of hyposulphite of soda, a considerable proportion of oxide of silver dissolves, and the liquid, when evaporated, yields crystals of the double hyposulphite of soda and silver. The chloride, bromide, and iodide of silver also dissolve readily in a solution of hyposulphite of soda, and after evaporation the liquid affords the same crystals of double hyposulphite. The solubility of the chloride, bromide, and iodide of silver is applied in photography, to the fixing of the image: that is, to the removal of the compounds of silver from the parts which have not been acted on by light. Solutions of the double hyposulphites when boiled give off sulphide of silver, and sulphate of soda is formed. The hyposulphite of silver can be obtained isolated, in the form of a white powder, by pouring a solution of hyposulphite of soda into a solution of nitrate of silver; but the precipitate soon blackens in the light, sulphide of silver being formed.

*Carbonate of Silver.*

§ 1122. Carbonate of silver, which is obtained in the form of a white precipitate, by pouring carbonate of soda into a solution of nitrate of silver, soon turns brown when exposed to solar light, and is readily decomposed by heat.

*Acetate of Silver.*

§ 1123. Acetate of silver is prepared by dissolving the carbonate in acetic acid, or by pouring acetate of soda into a concentrated hot solution of nitrate of silver; in which case the acetate of silver crystallizes in small prisms during the cooling of the liquid.



## COMPOUNDS OF SILVER WITH SULPHUR.

§ 1124. Silver and sulphur combine directly when a mixture of the two substances is heated. The excess of sulphur distils over, and if it be heated to redness, the sulphide of silver fuses and solidifies into a crystalline mass on cooling. Sulphide of silver corresponds to the protoxide: its formula is, consequently,  $\text{AgS}$ . It is found crystallized in nature in regular octohedrons, commonly modified by secondary facets, forming a blackish-gray mineral of a metalloid lustre, the density of which is 7.2. Sulphide of silver possesses a certain degree of malleability, and will receive impressions under the coining-press; but it is so soft that it can be scratched with the nail. Sulphide of silver is converted by roasting into sulphurous acid and metallic silver. Concentrated boiling chlorohydric acid decomposes it by disengaging sulphhydric acid and forming the chloride. Concentrated hot sulphuric acid also acts on it and converts it into a sulphate, the action of nitric acid yielding the same product. Sea-salt, protochloride of copper, and some other metallic chlorides convert the sulphide of silver into a chloride when assisted by heat.

The same sulphide of silver is produced, by the humid way, when a salt of silver is precipitated by sulphhydric acid, or by an alkaline sulphhydrate. Silver decomposes sulphhydric acid even when cold, especially in the presence of water, and its surface becomes covered with a black pellicle of sulphide. On account of which property, silver soon blackens in the vicinity of sulphuretted emanations; as for example, silver plate soon becomes tarnished when eggs or fish, or any kind of food which can evolve sulphhydric acid, is heated in it; especially when the articles are not very fresh.

Sulphide of silver combines with a great number of metallic sulphides, and principally with the electro negative sulphides, such as those of arsenic and antimony, forming double sulphides, many of which occur crystallized in nature.

Native sulphide of silver is isomorphous with native subsulphide of copper  $\text{Cu}_2\text{S}$ , and the two sulphides appear to possess the property of replacing each other in every proportion, as occurs for example, in the gray copper-ore or fahlerz. We have said that such isomorphism exists only between substances presenting the same chemical formulæ, and have frequently insisted on this law to establish the equivalents of simple bodies. But sulphide of silver would present an exception to the law if its formula was written  $\text{HgS}$ , that is, if the number 108 were adopted for the equivalent of the metal; which consideration has induced several chemists to assign to sulphide of silver the formula  $\text{Ag}_2\text{S}$ , that of  $\text{Ag}_2\text{O}$  to our protoxide of silver, and to take the number 54 for the equivalent of silver. This opinion is also confirmed by several other circumstances, on which we shall briefly dwell. It has been demonstrated by a great number

of experiments, that a very simple ratio exists between the specific heats of simple bodies and their chemical equivalents, and a law has been observed according to which *the specific heats of simple bodies are to each other nearly in the inverse ratio of their equivalents*. Now, silver only satisfies this law by admitting the number 54 for its equivalent. Moreover, an analogous law has been found for compound bodies, by which *the specific heats of compound bodies, of the same formula, are to each other very nearly in the inverse ratio of the numbers which represent their chemical equivalents*. Now, the sulphides of silver and copper  $\text{Cu}_2\text{S}$  satisfy this law, if the formula  $\text{Ag}_2\text{S}$  be admitted for the sulphide of silver.

But, if the formula of sulphide of silver be written  $\text{Ag}_2\text{S}$ , and, consequently, that of our protoxide of silver  $\text{Ag}_2\text{O}$ , the formula of soda should be written  $\text{Na}_2\text{O}$  and not  $\text{NaO}$ , as we have hitherto done; for we have seen (§ 1120) that sulphate of silver is isomorphous with anhydrous sulphate of soda. The salts of potassa and lithia being isomorphous with the corresponding salts of soda, when they contain the same quantity of water of crystallization, the formula of potassa should be written  $\text{K}_2\text{O}$  and that of lithia  $\text{Li}_2\text{O}$ ; which new formulæ are justified by the laws of specific heat, and by several important considerations. In fact, it has been found that the specific heats of the chlorides of potassium, sodium, silver, and the subchlorides of mercury  $\text{Hg}_2\text{Cl}$  and copper  $\text{Cu}_2\text{Cl}$ , are to each other in the inverse ratio of the equivalents of these substances. Now, there is no doubt that  $\text{Cu}_2\text{Cl}$  is the formula of subchloride of copper, on account of the indisputable isomorphism of the salts of the protoxide of copper  $\text{CuO}$  with the corresponding salts of the protoxide of iron, manganese, zinc, and nickel. The chlorides of potassium, sodium, and silver should, therefore, have formulæ similar to that of subchloride of copper  $\text{Cu}_2\text{Cl}$ , and these should be written  $\text{K}_2\text{Cl}$ ,  $\text{Na}_2\text{Cl}$ ,  $\text{Ag}_2\text{Cl}$ . On the other hand, potassa, soda, and lithia have hitherto presented no case of isomorphism with the oxides, the formulæ of which are written  $\text{RO}$ ; they never replace baryta, lime, magnesia, the protoxides of iron, manganese, zinc, etc., which circumstance becomes very natural if the formula  $\text{R}_2\text{O}$  is assigned to the alkaline oxides, but is not explained if the formula  $\text{RO}$  be retained.

Considering these circumstances, it appears that the equivalents of the alkaline metals ought to be reduced to their half: we have, however, been unwilling to make this change in the present work before it has been adopted by a majority of chemists.

## COMPOUND OF SILVER WITH CHLORINE.

§ 1125. Only one combination of silver with chlorine is known, corresponding to the protoxide. Chloride of silver  $\text{AgCl}$  is obtained by adding chlorohydric acid or a solution of sea-salt to the solution of any soluble salt of silver, when a white precipitate is formed, which soon collects, by shaking, in cheesy lumps, especially

VOL. II.—2 A

if the liquid contains an excess of nitric acid. Chloride of silver is nearly insoluble in water and in weak solutions of nitric acid, but dissolves sensibly in solutions of chlorohydric acid or the alkaline chlorides. Concentrated boiling chlorohydric acid dissolves a considerable quantity of chloride of silver, and the saturated solution deposits, on cooling, small octohedral crystals of the chloride. Ammonia is a very powerful solvent of chloride of silver, and the liquid, on being exposed to the air, gradually loses its ammonia and deposits octohedral crystals of chloride of silver, which frequently attain quite a considerable size. By saturating the ammoniacal liquid with nitric acid, the chloride of silver is again deposited. Solutions of the alkaline hyposulphites dissolve a large quantity of the chloride, (§ 1121.)

Chloride of silver fuses at about  $500^{\circ}$ , forming a yellow liquid, which, on solidifying, yields a translucent substance resembling horn, easily cut with a knife. At a red-heat, chloride of silver gives off appreciable vapours, although it is not sufficiently volatile to allow of distillation. It soon blackens in solar light. If the chloride be suspended in water, oxygen is given off, and, after some time, the liquid contains chlorohydric acid, while, if the chloride be dry, chlorine is disengaged: in both cases, by treating the altered substance with ammonia, chloride of silver is dissolved without colour, while metallic silver remains in the form of a black powder.

Chloride of silver absorbs, when cold, a large quantity of dry ammoniacal gas, giving rise to a compound, the composition of which is expressed by the formula  $\text{AgCl} + 3\text{NH}_3$ , and which readily parts with its ammonia by the application of heat. It has been shown (§ 123) that liquid ammonia can be obtained from this substance.

Chloride of silver is sometimes found crystallized in nature, forming cubic or octohedral crystals, of a pearl-gray colour when found in the interior of the rock, and of a more or less violaceous hue when occurring very near to or on the surface.

#### COMPOUND OF SILVER WITH BROMINE.

§ 1126. A bromide of silver  $\text{AgBr}$ , resembling the chloride, is obtained by pouring an alkaline bromide into a solution of nitrate of silver, in the shape of a white, slightly yellowish precipitate, which is insoluble in water and nitric acid, but readily dissolves in ammonia and the alkaline hyposulphites. Chlorine easily decomposes bromide of silver, and transforms it into chloride. Bromide of silver has been found native in certain silver-ores from Mexico.

#### COMPOUND OF SILVER WITH IODINE.

§ 1127. By adding iodide of potassium to a solution of nitrate of silver, a yellowish-white precipitate of iodide of silver  $\text{AgI}$  is obtained, which is insoluble in water, slightly soluble in nitric acid,

and soluble but to a small degree in ammonia, which properties serve easily to distinguish it from the chloride and bromide of silver. Chlorine decomposes it and sets the iodine free, and chlorohydric acid converts it into a chloride. It fuses below a red-heat. Although the effect of light on the iodide is less rapid than on the chloride, the former soon turns black, first assuming a brown tinge. Iodide of silver dissolves easily in a solution of iodide of potassium, and the liquid deposits, on evaporation, crystals of a double iodide  $\text{AgI} + \text{KI}$ . Native iodide of silver has been found in several silver-ores, in crystals belonging to the regular system.

#### COMPOUND OF SILVER WITH FLUORINE.

§ 1128. Fluoride of silver is obtained by dissolving the oxide or carbonate in fluohydric acid, forming a compound which is very soluble in water and partly decomposes by evaporation.

#### COMPOUND OF SILVER WITH CYANOGEN.

§ 1129. By adding a solution of cyanohydric acid to a solution of nitrate of silver, a white precipitate of cyanide of silver  $\text{AgCy}$  or  $\text{AgC}_2\text{N}$  is obtained, which is insoluble in water and dilute nitric acid, while chlorohydric acid decomposes it and converts it into a chloride. Ammonia dissolves it readily, and it is also easily soluble in the alkaline cyanides, with which it forms crystallizable double cyanides.

#### COMPOUNDS OF SILVER WITH CARBON.

§ 1130. Definite compounds of silver with carbon are obtained by decomposing by heat certain salts formed by the oxide of silver with organic acids. Two definite carburets have hitherto been observed, corresponding to the formulæ  $\text{AgC}$  and  $\text{AgC}_2$ . When heated in the air they become incandescent, and, after burning like tinder, leave metallic silver.

#### DETERMINATION OF SILVER, AND ITS SEPARATION FROM THE METALS PREVIOUSLY DESCRIBED.

§ 1131. Silver is determined either in the metallic state, or in that of the chloride, the first-named method being employed in the case of *cupellation*, a process presently to be described. When silver is in solution, it is generally precipitated by a slight excess of chlorohydric acid; and, in order to collect the precipitate more easily, it is better to employ a boiling solution to which an excess of nitric acid has been added. The clear supernatant liquid may be decanted off, and, if proper care be taken, none of the precipitate need be lost. In order to wash chloride of silver, it is poured into a thin porcelain capsule, filled with water slightly acidulated with nitric acid, and the liquid is heated to ebullition by means of an alcohol-lamp, the precipitate being kept suspended in the liquid by

stirring with a glass rod. After it has been allowed to rest, and the chloride has settled at the bottom of the capsule, the clear liquid is removed with a pipette and introduced into a cylinder, which process is repeated until the washing is completed. Lastly, any particles of chloride that may have found their way into the cylinder, are removed thence and added to that in the capsule, where the whole is dried; for which purpose, the capsule is placed upon another capsule heated by an alcohol-lamp, by which means a hot-air bath is obtained which completely dries the chloride. Finally, the capsule is weighed when cooled, and, the chloride being removed, the equilibrium is restored by weights. The dried chloride is sometimes fused in the capsule, in which case the separation, which is attended with some difficulty, is effected by boiling a small quantity of concentrated chlorohydric acid in the capsule containing the chloride, when the latter generally separates in a single mass. If it still adheres, water must be added, and a piece of zinc must be placed on the chloride, which, by being restored to the metallic state by the zinc, immediately separates.

The chloride of silver may also be collected in a very finely pointed glass tube, the aperture of which soon becomes closed, by small lumps of chloride, sufficiently to prevent the escape of any of the precipitate, without interfering with the filtration of the clear liquid. The chloride is washed in the tube, which is then dried in a stove. In all cases, chloride of silver should be washed in a room lighted by a lamp, so that it may not be affected by solar light.

§ 1132. The solubility of silver in nitric acid, and the complete insolubility of chloride of silver, renders the separation of this metal from all the metals previously described an easy matter. Silver cannot be immediately precipitated by chlorohydric acid, only in the case when it exists in solution with a subsalt of mercury, because a mixture of chloride of silver and chloride of mercury  $\text{Hg}_2\text{Cl}$  is deposited. But it is sufficient to treat the precipitate with boiling nitric acid, to which a few drops of chlorohydric acid have been added, to dissolve the mercury in the state of protochloride  $\text{HgCl}$ . The two metals may also be precipitated by sulfhydric acid, and the mixture of the sulphides roasted in the air, when the mercury volatilizes, while the silver remains entirely in the metallic state.

#### METALLURGY OF SILVER.

§ 1133. The most common ores of silver are:—

1. Sulphide of silver, either pure, or mixed with greater or less quantities of sulphide of copper  $\text{Cu}_2\text{S}$ , which do not change its crystalline form.

2. Sulphide of silver, combined with the sulphide of arsenic and antimony, forming a great number of minerals, to which mineralogists give different names; *e.g.*, sulfantimoniate of silver, of which the formula is  $3\text{AgS} + \text{Sb}_2\text{S}_3$ , and sulfarseniate of silver  $3\text{AgS} + \text{As}_2\text{S}_3$ .

These two minerals affect the same form of crystallization, clearly proving the isomorphism of the sulphides of arsenic  $\text{As}_2\text{S}_3$  and of antimony  $\text{Sb}_2\text{S}_3$ , which, however, is still better established in certain minerals containing at the same time sulphide of arsenic and sulphide of antimony in varying proportions  $6\text{AgS} + (\text{Sb}_2, \text{As}_2)\text{S}_3$ . Sulf-arsenates and sulfantimonates of silver are also found in which a portion of the silver is replaced by copper  $9(\text{Cu}, \text{Ag})\text{S} + (\text{Sb}_2, \text{As}_2)\text{S}_3$ .

3. The arseniuret of silver  $\text{Ag}_2\text{As}$ , and the antimoniuret  $\text{Ag}_2\text{Sb}$ .

4. The chloride, bromide, and iodide of silver, which are sometimes found in sufficient quantity to be worked as ores of silver.

5. Many galenas, and cupreous ores containing silver, are the most common ores of silver on the European continent.

6. Native silver, frequently scattered through the levellings of lead and argentiferous copper veins, and probably owing its presence to chemical reactions to which the ore has been subjected in the bosom of the earth, and which have removed the other metals in the state of soluble compounds, and left the metallic silver. Large masses of native silver are sometimes found, and at Konigsberg, in Norway, have been seen to weigh 280 kilogs.

§ 1134. Argentiferous lead-ores are first worked for their lead, from which, as it retains all the silver, the latter is separated by cupellation, (§ 987.) Argentiferous copper-ores are also worked for their copper, and the black copper resulting, is passed through a furnace with lead, furnishing an alloy, from which the argentiferous lead is separated by eliquation, (§ 1067,) and is subsequently subjected to cupellation. Again, the last coppery matts are subjected to an amalgamation, which shall soon be described.

Ores of silver which are too poor in lead or copper to be worked for the advantageous extraction of these metals, are immediately subjected to amalgamation, after having undergone a preliminary preparation. Two different methods of amalgamation are used—that of Freiberg, in Saxony, generally adopted in Europe, and the American method, which differs essentially from the European plan in requiring no fuel, and in being the only applicable method where fuel is scarce, as it is in Mexico and South America.

#### *Freiberg Process.*

§ 1135. The argentiferous ores of Saxony are composed of sulphide of silver combined or mixed with sulphides of arsenic, antimony, iron, zinc, etc. It is important that they should not contain more than 5 per cent. of lead, and, at most, 1 per cent. of copper, as these metals greatly interfere with the amalgamation: they amalgamate with mercury as readily as silver, and render the amalgam very tough. The various ores are sorted so that the charge shall contain 2 or 3 thousandths of silver and a proper quantity of pyrites, which latter are necessary, because, during the preliminary roasting, they furnish a certain proportion of oxide and sulphate of

iron, indispensable in the chemical reactions of amalgamation. They are to be added, if they do not exist in sufficient proportion; and sometimes a certain quantity of sulphate of iron is also added. Lastly, 10 or 12 parts of sea-salt are added to 100 parts of ore.

The mixture is roasted in a reverberatory furnace, heated at first very gently, in order to dry the material, which is then spread over the sole of the furnace, and the temperature being gradually raised, a red-heat is maintained for about 4 hours, when a large quantity of sulphurous acid is disengaged while the metals oxidize. The temperature being now raised still higher, sulphurous acid is disengaged anew, accompanied by vapours of sesquichloride of iron and chlorohydric acid, arising from the action of the steam and oxygen on the chloride of iron. After roasting for  $\frac{3}{4}$  of an hour, the roasted ore is withdrawn and thrown on a screen, where the consolidated fragments are retained, which are again ground, mixed with 2 per cent. of sea-salt, and subjected to a new roasting. The ore which has passed through the screen is again sifted, ground to an impalpable powder, bolted, and then sent to the amalgamating barrels.

During the roasting, the sulphides of iron and copper disengage sulphurous acid, oxides and sulphates being formed, while the sulphide of silver, being heated with the sulphates of iron or copper, is entirely converted into sulphate at the expense of the sulphates of iron and copper, which, while being transformed into oxides, cause the disengagement of sulphurous acid. The sulphates of iron and copper fuse together with the sea-salt before attaining a red-heat; and if the mixture contain sulphide of silver, sulphurous acid is disengaged by the reaction of the sulphur of the sulphides on the sulphuric acid of the sulphates, and the final products resulting from the roasting are thus, sulphate of soda, chloride of silver, and the chlorides of copper and iron. If the reaction takes place in the air, the iron passes partly into the state of sesquichloride and partly into that of sesquioxide; and the sulphides of arsenic and antimony are also

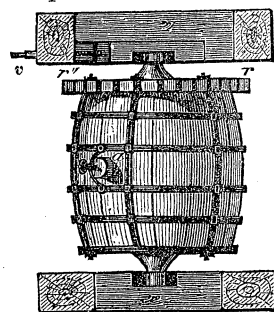


Fig. 586.

of the barrel. A cog-wheel  $rr''$  is attached to one end, working in

oxidized. As all these reactions take place during the roasting in the reverberatory furnace, the roasted ore may be admitted to consist, in addition to the quartzose gangues, of sulphate of soda, chloride of sodium, chlorides of manganese and lead, sesquichloride of iron  $Fe_2Cl$ , subchloride of copper  $Cu_2Cl$ , chloride of silver, and several metallic oxides.

The amalgamating barrels are made of wood, (fig. 586,) strengthened by iron hoops and bars, and the ends have iron plates, furnished with gudgeons exactly in the axis

another cog-wheel  $rr'$  (figs. 587 and 588) on a shaft AB turned by a water-wheel. Each barrel has a hole  $a$  closed by a bung kept in place by an iron stirrup. One of the pedestals on which the gud-

Fig. 587.

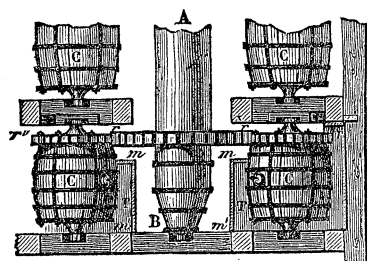
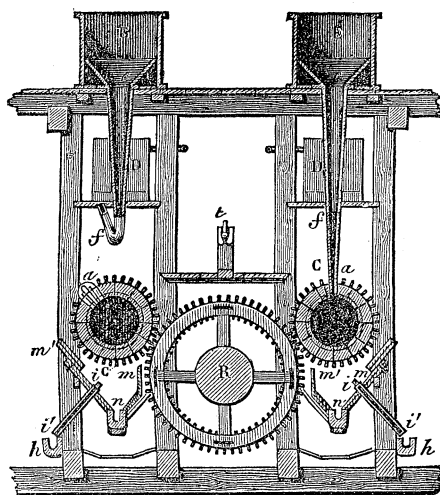


Fig. 588.

manner, they are made to revolve gently for 2 hours, after which each barrel is successively thrown out of gear, in order to allow of an examination of the consistence of the muddy substance it contains. If it is too tough, water is added; and if too liquid, more roasted ore is thrown in; and when the proper consistency is attained, 250 kilogs. of mercury are thrown into each barrel, and the whole is again set in motion, the temperature in the barrels rising considerably after some time, in consequence of the chemical reactions which take place in the mixture. After the barrels have revolved for 20 hours, at the rate of 20 revolutions a minute, they are stopped, completely filled with water, and made to revolve for 2 hours more, making 8 revolutions per minute, when the amalgam separates from the muddy substances, which have now become very

geons revolve is fixed, while the other is rendered movable by the screw  $v$ , so that the wheel  $rr''$  may be thrown into or out of gear without arresting the other barrels C, C placed near the horizontal staff A B, and working in the same cog-wheel  $rr'$ . Above each barrel is a box E containing the bolted ore, which is introduced into the former by means of a leather hose  $f$ , entering the opening  $a$ , while reservoirs D placed above each barrel contain the quantity of water necessary for a charge. Beneath the barrels are receivers  $mm'$ , intended to hold the material after the operation.

After 150 litres of water have been introduced into each barrel, the charge of ore, amounting to 500 kilogs., is inserted, being taken from the box E, while 50 kilogs. of scrap sheet-iron are added. The opening in the barrel is then closed with the bung, and when all the barrels are charged in the same



fluid. Each barrel being then successively thrown out of gear, and the bung turned downward, the small cork of the bung is removed, and as soon as all the amalgamated mercury has escaped and fallen into the receiver *mm'*, which is the case as soon as the mud appears, the workman replaces the cork. The mercury runs through the tube *ii'* into a canal *h*, which leads it into a particular reservoir. When all the mercury has escaped, the bung of the barrel is removed, the opening *a* turned downward, and the mud allowed to run into the box *mm'*, whence it flows into large reservoirs beneath, the scrap-iron being retained by a grate.

We have said that, before adding the mercury, the loaded barrels are turned for 2 hours: the intention of this is to decompose, during this period of the process, the sesquichloride of iron by the metallic iron, and restore it to the state of protochloride, because, if the mercury were introduced immediately, it would act on the sesquichloride of iron which it would reduce to protochloride, while a certain quantity of subchloride of mercury  $\text{Hg}_2\text{Cl}$  would be formed, which would decompose no longer, and occasion a considerable waste of mercury; all of which is avoided by first bringing the sesquichloride of iron to the state of protochloride. The chloride of silver, which dissolves in the solution of sea-salt, is decomposed by metallic iron, while the silver set free combines with the mercury; and the chlorides of copper and lead being decomposed in the same way by contact with the iron, these metals also amalgamate with the mercury. About 1 kilog. of iron is dissolved in each operation.

The mud escaping from the barrels is placed in tubs, where it is stirred by paddles attached to a vertical axis, after being diluted with a large quantity of water, the tubs being provided with openings at different levels, through which the muddy water escapes. A certain quantity of amalgam, which separates and falls to the bottom of the tubs, is then removed and added to that taken from the amalgamating barrels.

The mercury is filtered, with the assistance of slight pressure, through leather bags, through the pores of which, a small portion of liquid mercury, containing only a slight admixture of foreign metals, escapes; while a doughy amalgam, containing nearly 5 parts of mercury and 1 part of silver, mixed with foreign metals, remains in the bags. The mercury is separated from the amalgam by distillation, which is effected by various kinds of apparatus, of which it will suffice to describe the most simple one. To the opening of the cast-iron tube *ab*, (fig. 589,) which is closed at one end *a*, and has been charged with

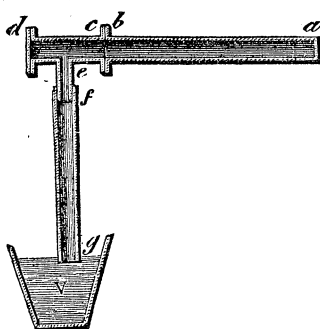


Fig. 589.

about 150 kilogs. of amalgam, is fitted a bent tubing *cde*, the tubulure *e* of which enters a sheet-iron tube *fg*, which dips slightly into the water contained in the receiver *V*. The tube *ab* being gradually heated to redness, the mercury distils and condenses in the receiver *V*, while the silver, mixed with a greater or less quantity of copper and lead, remains in the tube *ab*.

*Amalgamation of the Cupreous Matts by the Mansfeld Process.*

§ 1136. Amalgamation is applied to the last cupreous matts arising from the process described, (§ 1066). The matt is stamped and sifted, and then ground to an impalpable powder, which is moistened with a small quantity of water and roasted in a reverberatory furnace. The furnace, a vertical section of which is seen in fig. 590, has generally 2 stories, surmounted by condensing chambers

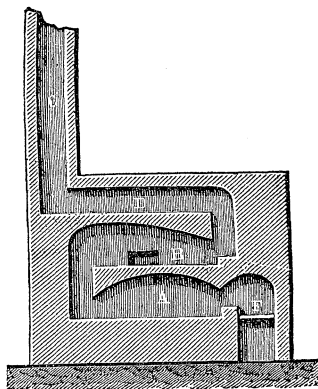


Fig. 590.

where the vapours and dust carried over are retained. The matt is first roasted in the upper space *B*, while in the lower space *A* a charge is being roasted, consisting of about 200 kilogs. of matt, spread in a thin layer over the sole. A very high temperature is not applied, because it is indispensable to prevent the softening of the substance, which would interfere with the roasting. The workman stirs the material with an iron rake, in order to renew the surfaces exposed to the oxidizing action of the air, and the roasting lasts about 3 hours, after which the material is removed with an iron scoop and

dropped into a box. After the first roasting, the material is mixed with 9 or 10 per cent. of sea-salt and 10 per cent. of very finely powdered limestone; water is added, and the whole is worked into a homogeneous paste, which is dried in stoves. The mass is again ground to powder and roasted in a lower furnace *A*, where a higher temperature prevails.

The limestone is added to decompose a portion of the sulphates of iron and copper; which, if present in too great quantity for amalgamation, would occasion a waste of mercury. When the workman supposes that the material is sufficiently prepared, he proceeds to test it by mixing a small quantity of the roasted powder with water and mercury, and, after diluting it with a larger quantity of water, separating a mercurial amalgam, the nature of which he estimates by its physical properties. According to the appearance of the amalgam, he adds a small quantity of salt, lime, or even of roasted matt.

The second roasting lasts only about  $1\frac{1}{2}$  or 2 hours.

The material thus prepared is poured into the amalgamating barrels, which resemble those of Freiberg, 500 kilogs. of roasted material, 150 litres of hot water, and 40 kilogs. of scrap-iron being introduced into each barrel. After having caused the barrels to revolve for some time, 150 kilogs. of mercury are added, and then the barrels are made to turn at the rate of 15 revolutions per minute for 14 hours. 100 litres of water are then added to each barrel, which is turned gently for some time to facilitate the separation of the amalgam.

The deposit of cupreous matt which remains after the complete separation of the amalgam, after being mixed and pounded with 15 per cent. of clay, is made into lenticular cakes, which are smelted, after drying, in a furnace, with the addition of quartz, furnishing black copper, which is subsequently refined, (§ 1068.)

The amalgam of silver is treated in the same way as at Freiberg.

#### *American Process.*

§ 1137. The principal mines in America are those in Mexico and Chili, which furnish ores consisting of metallic silver, sulphide of silver isolated or combined with sulphides of arsenic and antimony, chloride of silver, etc., these minerals being generally disseminated in such fine particles as not to be perceived in the gangue.

The ores are first stamped, then ground to a fine powder, and made into heaps, called *tarts*, (*tourtes*), containing 500 to 600 quintals, on platforms built of stone. The material, after being moistened with water, to which 2 to 5 per cent. of sea-salt are added, is rendered homogeneous by being stamped by horses or mules. In a few days, about  $\frac{1}{2}$  or 1 per cent. of *magistral* is added to it, consisting of a roasted copper pyrite, containing 8 to 10 per cent. of sulphate of copper. It is again stamped, and the first portion of mercury added; and when this has been well disseminated through the mass, a small portion of the material is washed in a wooden bowl to separate the amalgamated mercury. By its appearance the workman judges if it be necessary to add lime or magistral. If the surface of the amalgam is grayish and the metal agglomerates easily, the amalgamation is going on correctly; but if the mercury is much divided, and its surface exhibits a dark colour with brown spots, the magistral is in excess, and the tart is then said to be *too hot*. As a continuation of the process under these conditions would occasion a great loss of mercury, lime is added, which decomposes a portion of the sulphate and chloride of copper produced by the reaction. If, on the contrary, the mercury retains its fluidity, the chemical reactions do not advance, and the tart, being *too cold*, must be heated by the addition of magistral.

After about 15 days, when the first portion of mercury has combined with a sufficient quantity of silver to be converted into a doughy amalgam, a second portion of mercury is added; and when

this is well incorporated with the mass, a third and last addition is made; the test just described being frequently repeated, in order to judge of the progress of the operation. The whole process lasts 2 or 3 months, according to the nature of the ore and the temperature. When it is finished, the material is washed in water to separate the amalgam from it, which is filtered through cloth, and the solid part which remains is distilled. By the American process, 1 to 3 parts of mercury are lost for 1 part of silver obtained.

The following is the theory of the operation:—The sea-salt and sulphate of copper of the magistral usually decompose each other, protochloride of copper  $\text{CuCl}$  and sulphate of soda being formed, while the metallic silver decomposes the protochloride of copper, and, by restoring it to the state of subchloride  $\text{Cu}_2\text{Cl}$ , is itself converted into chloride of silver. The subchloride of copper dissolves in the solution of sea-salt, and reacts on the sulphide of silver, forming sulphide of copper and chloride of silver. The mercury, in its turn, acts on the chloride of silver, which dissolves in a solution of sea-salt, forming subchloride of mercury  $\text{Hg}_2\text{Cl}$ , while the metallic silver combines with the rest of the mercury. It is necessary, in this operation, as in the Freiberg process, that no free protochloride of copper should remain, because this would increase the waste of mercury, by parting with one-half of its chlorine to the latter metal in order to transform it into subchloride  $\text{Hg}_2\text{Cl}$ . The intention of the addition of lime is to decompose the chloride of copper in excess, and destroy the bad effects of an excess of magistral. The subchloride of copper  $\text{Cu}_2\text{Cl}$  exerts no injurious influence.

#### REFINING OF SILVER ARISING FROM CUPELLATION OR AMALGAMATION.

§ 1138. The impure silver is melted, exposed to a current of air which oxidizes the foreign metals, in a furnace consisting of a hemispherical cast-iron cavity, lined with a thick coat of marl or wood-ashes, which forms a sort of porous cupel, serving to absorb the liquid oxides produced by the oxidation of the foreign metals. The cavity is filled with charcoal, on which the silver to be refined is placed, and the combustion is assisted by a bellows, which, at the same time, furnishes the air necessary for oxidation. When the silver has become liquid in the cupel, the air is projected over the surface of the bath until no spots form on its surface, and the metal, being then refined, contains at most 1 per cent. of foreign matter.

#### *Alloys of Silver.*

§ 1139. Silver is rarely used in a state of purity, as it is too soft, and articles made of it would soon be worn and lose the sharpness of their edges and angles. It is generally alloyed with a certain quantity of copper, which increases its hardness; and the alloy does not assume a decided yellow tinge unless a considerable quantity

of copper is present, more than  $\frac{1}{8}$  being necessary to destroy the white colour, to which, as it is less fresh than that of pure silver, the brilliancy of the latter is artificially given, by a process called *washing*. The intention of this operation is to remove the copper which is immediately on the surface of the alloy; for which purpose the article is heated to a dull red-heat, when the superficial layer of copper oxidizes, and by plunging it immediately into water, acidulated by nitric or sulphuric acid, the oxide of copper dissolves. After the washing, the surface of the article is necessarily dead, because the particles of silver are, as it were, separated from each other; but it is readily polished by burnishing.

Alloys of silver for coin, jewelry, and plate are subjected to a legal standard, regulated by law, and secured by a stamp for jewelry and plate.

The standard of French coin is  $\frac{900}{1000}$ , that is, it must contain 900 of silver and 100 of copper; but as the exact proportions cannot always be obtained, a variation of  $\frac{3}{1000}$  is allowed. Thus an alloy of 897 of silver and 103 of copper is received, while an alloy of 896 of silver and 104 of copper is illegal. Alloys containing more than 903 of silver are not admitted, as it is more advantageous to melt them again with a small quantity of copper, to reduce them to the legal standard.

The standard of silver medals is  $\frac{950}{1000}$ , with a variation of  $\frac{3}{1000}$  as for coin.

The ordinary standard of jewelry and plate is  $\frac{950}{1000}$ , but the variation is greater than in coin, being allowed to reach  $\frac{5}{1000}$  below. No superior limit is fixed, because it is not the interest of the silver-smith to exceed the legal standard.

The solder used for silver plate consists of 667 parts of silver, 233 of copper, and 100 of zinc.

§ 1140. Many articles are made of sheet-copper covered with a lamina of silver, and are then called *plated-ware*, the ordinary standard of which is  $\frac{1}{20}$ , that is, the sheet should be composed of  $\frac{19}{20}$  of copper and  $\frac{1}{20}$  of silver; while sometimes, however, an inferior standard is adopted. Plated-ware is made in the following manner:—A plate of copper, and one of silver having the same surface and weighing  $\frac{1}{20}$  of the copper, being selected, the surface of the copper is carefully scraped, and it is then dipped into a strong solution of nitrate of silver, where it is covered with a thin coat of metallic silver. This being done, the silver plate is applied to the copper, and, the whole being heated to a brownish-red colour in an oven, is then passed through a roller until the sheet has attained the required thickness. The two metals adhere so strongly as to defy mechanical separation.

## ASSAY OF ALLOYS OF SILVER.

§ 1141. It is important to be able to ascertain quickly and exactly the standard of alloys of silver, in order that the manufacture of coin and silver plate shall remain under protection of the government. The assay is made in two ways: the first, and older, by *cupellation*; and the second, by analysis by *the humid way*, which latter process, being much more exact, has taken the place of cupellation in the government assay-office.

*Assay by Cupellation.*

§ 1142. The analysis of alloys of silver and copper by cupellation is founded on the property of silver not to oxidize when kept in a fused state in the air, and to yield nearly insensible vapours; while copper, on the contrary, oxidizes under these circumstances, and is converted into the suboxide  $\text{Cu}_2\text{O}$ ; but, in order to separate this substance from the alloy, it has been found necessary to introduce into the latter a certain quantity of lead, which, by oxidizing, produces liquid litharge in which the suboxide of copper dissolves.

Fig. 591.



Fig. 592.



The roasting is effected in a *cupel*, (fig. 591,) that is, in a thick porous capsule made by compressing bone-ashes, slightly moistened with water, in moulds, where it takes the shape of which a vertical section is seen in fig. 592. The fused oxide of lead, which holds the other oxides in solution, soaks into the cupel, and nothing remains at last in the latter but the globule of refined silver. A cupel of bone-ash can absorb about its own weight of litharge.

The quantity of lead necessary to add to an alloy of silver and copper, to effect its easy cupellation, should be in proportion to the quantity of copper contained; because the litharge, after having dissolved the suboxide of copper, which is simultaneously formed, must preserve sufficient fluidity to soak readily into the cupel. If the infiltration does not ensue, the metal becomes covered with litharge and oxidation ceases, in which case the assay is said to be *drowned*, (*noyé*.)

Assay by cupellation is generally performed upon 1 gramme of alloy; and experience has shown that the following quantity of lead must be added according to the standard of the alloy.

Standard of the Alloy.		Lead necessary for refining 1 gramme of silver.
Silver at	1000.....	0.5 gm.
"	950.....	3
"	900.....	7
"	800.....	10
"	700.....	12
"	600.....	14

VOL. II.—2 B

Standard of the Alloy.		Lead necessary for refining 1 gramme of silver.
Silver at	500.....	} 16 to 17 gm.
"	400.....	
"	300.....	
"	200.....	
"	100.....	
Pure copper.....		

The standard of the alloy, of which the exact composition is to be ascertained, being in general approximately known, an inspection of the table, therefore, gives immediately the quantity of lead to be added. Supposing, for example, that the standard of a piece of coin is to be exactly determined; knowing that its standard must be nearly  $\frac{900}{1000}$ , an addition of about 7 gm. of lead must be made to 1 gm. of alloy very exactly weighed.

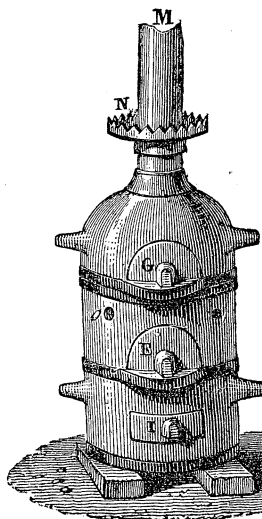


Fig. 593.

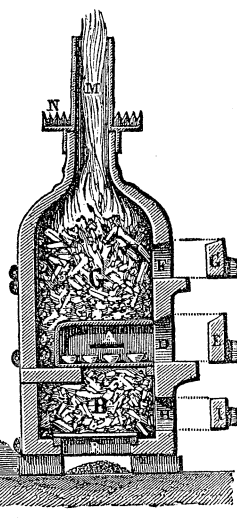


Fig. 594.

Fig. 593 represents a cupelling-furnace, of which a vertical section is seen in fig. 594. The *muffle* A, which is the most important part of the furnace, is a semi-cylindrical earthen cradle (fig. 595) closed at one end, and arranged in the furnace so that it can be entirely surrounded with fuel, and its opening corresponds exactly to the aperture D of the

furnace. The sides of the muffle are furnished with longitudinal slits, through which the external air which enters at the mouth of the muffle escapes into the current of air in the furnace; by which arrangement the muffle is constantly traversed by a very oxidizing current of air. The reverberatory furnace has generally a sheet-iron pipe M to increase its draught.

The furnace being filled with charcoal through the hole F, the cupels are introduced into the muffle, after having been previously dried on the platform N, if newly made. When the cupels are in the muffle, the opening D is closed with the door E, in order to raise the



Fig. 595.

temperature in the muffle, and when this is done the aperture D is opened, through which the portion of lead to be added to each assay is dropped into each cupel. As soon as the lead is in fusion, the *assay* (prise d'essai) is introduced, when the metals soon melt, while the alloy of silver dissolves entirely in the lead; and in a few moments the alloy forms in each cupel a round liquid globule. White vapours, arising from the oxidation of the metallic lead in the air, are soon disengaged, and the surface of the metallic globule is covered with a pellicle and fine drops of fused oxide, which move rapidly over its surface. The oxides gradually soak into the cupel, and when the lead and copper are completely converted into oxides and absorbed by the bone-ash, the silver is refined, and the motion on its surface ceases; the phenomenon of *lightning*, as described § 997, being produced on a small scale. The cupel must then be brought slowly to the opening of the muffle, in order that the globule of silver may not be too rapidly cooled. It has been mentioned (§ 1115) that pure silver absorbs a certain quantity of oxygen from the air, and that the absorbed gas is suddenly disengaged at the moment of solidification, while the metal is cooling rapidly, causing a sudden evolution of gas by which a small quantity of the metal is generally projected from the vessel, in which case the silver is said to *sputter*, (roche.) It is easy to tell by the appearance of the button, when cooled, whether a sputtering has taken place, as in that case a kind of vegetation, like a little mushroom, may always be seen at the places where the gas has escaped; and all assays presenting this character should be rejected, as they necessarily imply too small a quantity of silver.

In order that the assay may be admitted, the globule should be slightly adherent to the cupel, its lower surface should appear very smooth and of a dead colour, and the upper surface polished and free from roughness. When the upper surface is dull and furrowed, it proves either that the silver has sputtered, that the refining has been imperfect because the temperature has been too great, or that there was too little lead.

§ 1143. As the temperature of the furnace exerts great influence over the cupellation, the assay always presents some degree of uncertainty, and the assayer is, in fact, between two difficulties: if the temperature rises too high, the silver is perfectly refined, but there is considerable loss from volatilizing, and a small quantity of silver is carried into the cupel by the litharge, which, in that case, is very fluid; while, if not heated sufficiently high, the loss of silver is less, but the refining is imperfect, and the globule retains a small quantity of lead. These two causes of error exist simultaneously in all assays, and neutralize each other more or less completely; and, accordingly, as one or the other predominates, the standard will be found too low or too high.

The assayer should always endeavour to heat his furnace in the



same manner, and he can then construct a table by which he knows, for each alloy, the correction which should be made in each assay in order to obtain the exact standard. A table of this kind, which is made by cupelling alloys of known proportions, obtained by melting, with a proper quantity of lead, determinate proportions of silver and copper, can be of use only to the assayer who has made it, and who always operates with the same furnace. As a measure of greater certainty, the assayer, from time to time, performs a cupellation on a *trial-piece*, (*témoin*,) that is, on an alloy the composition of which he knows *à priori*, in order to ascertain whether the assay yields a loss equal to that indicated by his table. If otherwise, he modifies the results of all the assays simultaneously made, in the manner suggested by the assay of the trial-piece. We subjoin the table adopted in the Mint at Paris, according to the standard of the alloys:

Real Standards.	Standards found by cupellation.	Waste, or quantities necessary to add to the standard obtained, in order to produce the real standard.
1000.....	998.97.....	1.03
950.....	947.50.....	2.50
900.....	896.00.....	4.00
850.....	845.85.....	4.15
800.....	795.70.....	4.30
750.....	745.48.....	4.52
700.....	695.25.....	4.75
650.....	645.29.....	4.71
600.....	595.32.....	4.68
550.....	545.32.....	4.68
500.....	495.32.....	4.68
400.....	396.05.....	3.95
300.....	297.40.....	2.60
200.....	197.47.....	2.53
100.....	99.12.....	0.88

When the cupellation has been carefully performed, the true composition may be ascertained within 2 or 3 thousandths.

The lead used in cupellation, which should be as free as possible from silver, is called in commerce *assay-lead*. In all cases, the assayer should ascertain previously the purity of his lead by a preliminary assay.

#### *Assays by the Humid Way.*

§ 1144. Assays by the humid way are made by precipitating silver in the state of insoluble chloride by a standard solution of common salt. As chloride of silver readily aggregates by agitation, in a liquid acidulated with nitric acid, the exact moment when precipitation of silver no longer takes place may be easily ascertained. The solution of salt used being such that 1 cubic diameter of the

liquid exactly precipitates 1 gm. of pure silver, the standard of an alloy is determined by dissolving 1 gm. of it in 5 or 6 gm. of nitric acid, and carefully pouring the solution of salt into the liquid until precipitation ceases after the addition of one drop. After each addition of the saline solution, when the moment of complete precipitation approaches, the bottle containing the solution of silver must be shaken in order to aggregate the precipitate and clear the liquid. The number of cubic centimetres necessary to completely precipitate the silver gives the standard of the alloy.

The process may be simplified and brought to great exactness when it is applied to the exact determination of the standard of an alloy of which the approximate value is known; for example, of a piece of silver coin or plate. Two solutions of sea-salt are then used: one, which is called the *normal solution*, and which is such that 1 decilitre precipitates exactly 1 gm. of pure silver; and another, called the *decimal liquid*, which is 10 times more dilute, and of which 1 litre is required to precipitate 1 gm. of silver. Lastly, a third standard solution is sometimes used, called the *decimal solution of silver*, which contains 1 gm. of silver in 1 litre.

Supposing that the standard of a piece of coin is to be ascertained, consisting of an alloy which must contain, at least,  $\frac{897}{1000}$  of silver, but which we will assume to contain only  $\frac{896}{1000}$ ; then, according to the latter composition, 1.116 gm. of alloy contains 1 gm. of silver. After having dissolved 1.116 gm. of alloy, very exactly weighed, in a ground-stoppered bottle, by means of 5 or 6 gm. of pure nitric acid, 1 decilitre of the normal solution of sea-salt is poured into the bottle. It is evident that, if the standard of the alloy be really  $\frac{896}{1000}$ , the silver will be completely precipitated, and the liquid will not contain an excess of salt, while, if the standard be higher, silver still remains in solution, and if lower, the silver has been completely precipitated, but there is an excess of salt in the liquid. In order to ascertain this, the bottle is corked and shaken quickly, in order to clear the liquid, after which one cubic centimetre of decimal saline solution is added, which can precipitate 1 thousandth of silver. If silver is still contained in the liquid, a very perceptible white cloud is formed, and the bottle being then again shaken, a second cubic centimetre of decimal solution is added. If a precipitate be produced, the same process is repeated until the liquid remains clear. Supposing that 5 cubic centimetres of the decimal solution, gradually added, have produced precipitates, but that the 6th cubic centimetre has not affected the transparency of the liquid, it will be hence inferred, that after the precipitation of 1 gm. of pure silver by the cubic decimetre of the normal solution of salt, the liquid contained, at least, 4 thousandths of silver. The fifth cubic centimetre of decimal solution having produced cloudiness, while the 6th did not, it is evident that the liquid did not

contain more than 5 thousandths of silver, and, by assuming  $4\frac{1}{2}$  thousandths, we are sure of having found the amount of silver contained in the alloy within nearly  $\frac{1}{2}$  thousandth. The real standard of the alloy is, therefore,  $896 + 4\frac{1}{2}$ , or  $900\frac{1}{2}$  thousandths.

If the first cubic centimetre of a decimal saline solution does not yield a fresh precipitate in the solution of silver which has already received the cubic decimetre of normal saline solution, it is evident that the standard of the alloy is not above  $\frac{896}{1000}$ , and that, consequently, it should be rejected.

The exact composition of the alloy may be determined by means of the decimal solution of silver, always beginning by adding one cubic centimetre of the latter, which precipitates the cubic centimetre of decimal saline solution which had been added, and which must be neutralized. The liquid being cleared by agitation, one more cubic centimetre of decimal solution of silver is added, and if cloudiness be produced, the bottle is again shaken before a second cubic centimetre of the same liquid is added, which process is continued until the addition of another cubic centimetre of the decimal solution of silver no longer clouds the liquid. Supposing that the first three cubic centimetres have yielded precipitates, but that the liquid remains clear on the addition of the fourth, it is very probable that the third cubic centimetre has not been entirely decomposed, and

it may be admitted that one-half of it has been useless, and that  $2\frac{1}{2}$  cubic centimetres of the decimal solution of silver have sufficed to decompose the salt which remained free after the addition of the cubic decimetre of the normal saline solution; for which reason  $2\frac{1}{2}$  thousandths must be subtracted from the standard  $\frac{896}{1000}$ , thus leaving for the exact standard of the coin examined  $\frac{893.5}{1000}$ .

We shall now briefly describe the assaying apparatus used in the Mint at Paris, where these assays are daily made.

The normal solution of salt is contained in a copper vessel V, (fig. 596,) tinned on the inside, and completely closed to prevent evaporation, which would alter the standard of the liquid, only a Mariotte's tube *uv* allowing the entrance of air. The vessel, which is fixed in the upper part of the laboratory, has a curved tube *cde*, with a stopcock *r*, and to the lower part of which the pipette A, which measures exactly 1 decilitre of normal solution, is

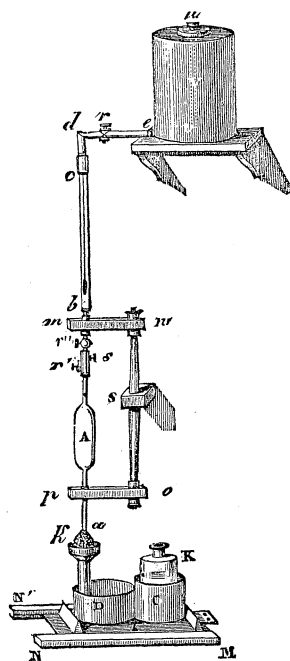
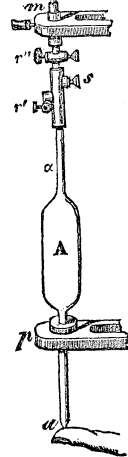


Fig. 596.

connected by means of a tube *bc* which contains a thermometer. The metallic piece which connects the glass tube *bc* with the pipette (fig. 597) has two stopcocks *r'*, *r''*, the one of which shall presently

be explained. The assayer having closed the end *a* of the pipette with his finger, opens the stopcocks *r'*, *r''*, thus allowing the saline solution to flow in a thin stream into the pipette, without stopping the upper tube of the latter, so that the air contained in the pipette can escape freely through the stopcock *r'* and the small tubulure which terminates it. When the pipette is filled a little above the mark *a*, the assayer closes the stopcocks *r'* and *r''*.



The bottle which contains the alloy dissolved in nitric acid is placed in the compartment C of a support I, (fig. 596,) which slides between the grooves MN, M'N', and which is provided with an appendix D, furnished at its upper part

Fig. 598.

with a small sponge *k*, placed at the height of the lower orifice *a* of the pipette. The assayer having so placed the support as to bring the sponge in contact with the pipette, opens the stopcock *r'*, and allows the liquid to descend slowly to the level *a*, where the sponge absorbs the last drop of liquid, which would adhere to the end of the pipette. The assayer then brings the opening of the bottle under the pipette, and empties it entirely by opening the stopcock *r'*.

As a large number of assays is generally made at once, there are a series of bottles numbered, in each of which are dissolved 1.116 gm. of alloy of coin. In order to hasten the solution, all the bottles are placed on a stand, (fig. 598,) and after having introduced into each the alloy and the nitric acid which is to dissolve it, the stand is plunged into hot water. When the metals are dissolved the nitrous vapours are driven off by blowing into the bottles, and the decilitre of normal solution is introduced, after which they are placed on a second stand, (fig. 599,) suspended on a steel spring, and held below by a spiral spring

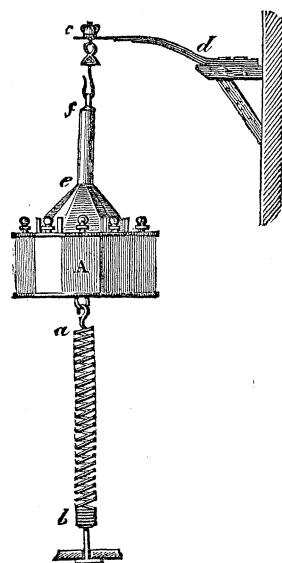


Fig. 599.

*ab.* The bottles having been closed by their ground stoppers, the assayer grasps the handle *ef* of the stand and shakes it for a few moments, in order to collect the precipitate and render the liquids

clear. He then carries the bottles to a black table having numbered compartments, each one being placed in the compartment corresponding to its number. The decimal solution is contained in a bottle (fig. 600) provided with a tube, drawn out at its lower extremity and having a mark corresponding to a capacity of 1 cubic centimetre, which dips into the liquid. The assayer, applying his finger to the upper aperture of the tube, withdraws the latter, and allows the liquid to flow slowly until it reaches the level of the mark, and then carries the



Fig. 600.

cubic centimetre thus measured off into the first bottle, repeating the process with the other bottles. He then examines the bottles successively, and makes with chalk a mark on the black table near each bottle in which a precipitate is formed, and then replaces the bottles on the stand of fig. 599, clears the liquids by agitation, deposits the bottles on the table, and adds another cubic centimetre of the decimal solution to all the bottles in which there was previously a precipitate formed, gradually excluding the bottles in which the liquid was not clouded. By counting the number of chalk-marks near each bottle, a number which represents that of the cubic centimetres of decimal solution which have been efficient, and deducting  $\frac{1}{2}$  for the last cubic centimetre, which, probably, has not been wholly used, the assayer finds the number of thousandths which must be added for each alloy to the supposed standard of  $\frac{896}{1000}$ .

As the standard solution of sea-salt has been prepared for the temperature of 59° degrees, and as it expands by heat, it is evident that its standard must be altered in volume by the changes of temperature. It is therefore indispensable, when the temperature of the solution is not 59°, to correct all the results by means of tables made for the purpose, the temperature of the saline solution being read off on the thermometer contained in the tube *cb*, (fig. 596.) But the corrections are always uncertain, and may be avoided by the following device, by means of which, at the same time, any wrong preparation of the normal solution is ascertained. An assay upon 1 gm. of pure silver, made daily, simultaneously with the tests on the coin, gives for each day the exact value of the standard of the normal saline solution, and all assays made simultaneously may be corrected by the difference of the standard thus found with the normal standard.

A large quantity of normal solution of salt is generally made at once, by dissolving 500 gm. of common impure salt of commerce in 4 litres of water, filtering the liquid, and adding the quantity of water necessary to obtain the necessary degree of dilution of the normal solution, supposing the salt to be pure; by which means a solution is obtained of a degree of concentration only approximative to that desired. In order to ascertain its exact concentration, 1 cubic decimetre of the liquid is poured into a solution of 1 gm. of pure silver in nitric acid. The liquid being cleared by agitation, it

is easy, by means of a decimal saline solution or a decimal solution of silver, to determine exactly the number of thousandths of silver, or of salt, which remain free. The additional quantity of water or salt necessary to obtain the proper dilution of the saline solution is thus found, and, after it has been added, a new test is made, and so on, until the normal degree of concentration is attained.

In order to prepare the decimal solution, a decilitre of the normal solution is introduced into a bottle which measures 1 litre to a mark traced on its neck, up to which the bottle is then filled with distilled water.

The decimal solution of silver is prepared by dissolving 1 gm. of pure silver in 5 or 6 gm. of nitric acid, and diluting with water until the liquid exactly assumes the volume of 1 litre.

When silver contains mercury, the results of the assay by the humid way are inaccurate, because the mercury, being precipitated in the state of chloride, decomposes a portion of the chloride of sodium. The presence of any considerable quantity of mercury in an alloy is easily perceived, because the liquid, in that case, is not cleared by shaking, and the first deposit of chloride of silver does not blacken in the light. The exact standard of the alloy may, however, be obtained by the humid way, by recommencing the test on another portion of the substance after having added a certain quantity of acetate of soda to the nitric solution, by which means the precipitation of the mercury is prevented.

#### ASSAYING OF SILVER ORES.

§ 1145. The argentiferous galenas are assayed by cupelling the lead, after having isolated it by the process described § 980. The galena is sometimes also fused with 3 or 4 tenths of its weight of nitre, when the sulphur of the galena is converted into sulphuric acid which combines with the potassa, while the greater portion of the lead separates in the metallic state, retaining the whole of the silver.

The argentiferous copper-ores are first assayed for their copper, after which the lump of copper is introduced into the cupel, with the addition of 16 times its weight of lead.

The assay for copper is made as follows:—If the ore be sulphuretted, it is first roasted in a small earthen capsule, (called *tile* in England,) the heat being properly regulated in order to prevent the substance from running together, and the temperature being kept elevated until sulphurous acid is no longer disengaged. The tile being then covered with its lid, the temperature is raised to a white-heat, in order to decompose the sulphates; after which the roasted material is fused in an earthen crucible with 3 or 4 times its weight of black flux, the fusion being effected in a forge-fire or an ordinary calcining furnace, having a strong draught. After cooling, the crucible is broken, and a lump of malleable copper and an

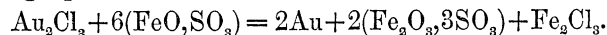
alkaline slag containing merely a trace of copper are found. Oxidized copper-ores need not be previously roasted, but can be immediately subjected to the fusion with black flux.

Oxidized silver-ores are mixed with 8 or 10 times their weight of litharge and double their weight of black flux, and the mixture is fused in an earthen crucible, when a portion of the litharge is converted, by the carbon of the black flux, into metallic lead, which carries with it all the silver; the quartzose and earthy gangues being transformed into slag with the litharge and potassa of the black flux. Ores of silver which contain sulphides and arseniurets are also fused with litharge, but it is in this case frequently unnecessary to add black flux, because the reaction of the sulphides and arseniurets on the litharge furnishes a sufficient quantity of metallic lead to entirely remove the silver.

## GOLD.

$$\text{EQUIVALENT} = 98.5 (1231.25; \text{O} = 100).$$

§ 1146. The gold in gold coin and jewelry is never pure, being alloyed with a certain quantity of copper and frequently of silver, to give it a greater degree of hardness. In order to obtain pure gold, gold coin is dissolved in aqua regia, and the solution being evaporated to dryness, by gentle heat, to drive off the excess of acid, the residue is treated with water, by which means the silver is separated as insoluble chloride. An excess of protosulphate of iron, which precipitates the gold in the metallic state, in the form of brown powder, is then poured into the liquid, the reaction ensuing according to the following equation:



The precipitate is digested with weak chlorohydric acid, and, after being well washed, is fused in an earthen crucible with a small quantity of borax and saltpetre. The protosulphate of iron may be replaced by sesquichloride of antimony  $\text{Sb}_2\text{Cl}_3$  dissolved in an excess of chlorohydric acid; the sesquichloride of antimony being converted into the perchloride  $\text{Sb}_2\text{Cl}_5$ , while the gold is precipitated in the metallic state.

Gold has a characteristic yellow colour, and its density is 19.5. It fuses at a strong white-heat, or at about  $2200^\circ$  of the air thermometer, giving off sensible vapours at a very high temperature. A gold wire is converted into vapour when traversed by the current of a powerful electric battery; and if this take place over a sheet

of paper placed at a small distance, the paper becomes coloured of a purplish brown, by the very finely divided gold which is precipitated on it. A blade of silver substituted for the paper soon becomes gilded. A globule of gold gives off vapour very copiously when held between two pieces of charcoal terminating the conductors of a powerful galvanic battery.

Gold is the most malleable of all the metals, (§ 295,) and when beaten into very thin leaves is transparent, the transmitted light appearing of a beautiful green colour. Gold may be crystallized by fusion, when it assumes the shape of cubes modified by other facets of the regular system. Native gold is sometimes found in well-defined crystals presenting the same form.

When precipitated in a metallic state from its solutions, gold forms a brown powder, which by burnishing soon recovers the metallic lustre and characteristic colour of malleable gold, and which aggregates by percussion. If the mass be heated to redness before being hammered, a perfectly aggregated metal can be obtained without having heated it to fusion.

Gold does not combine directly with oxygen at any temperature. Chlorohydric, nitric, and sulphuric acids do not affect it, while aqua regia, on the contrary, readily dissolves it in the state of sesquichloride,  $\text{Au}_2\text{Cl}_3$ . Gold is also dissolved by chlorohydric acid when a substance capable of disengaging chlorine is added, such as peroxide of manganese, chromic acid, etc. Chlorine and bromine also attack gold, even when cold, while iodine acts on it but feebly.

Sulphur does not attack gold at any temperature, nor does the metal decompose sulphydric acid; but by fusing it with the alkaline polysulphides it is powerfully acted on, a double sulphide being formed, in which the sulphide of gold  $\text{Au}_2\text{S}_3$  acts the part of a sulph-acid. Arsenic when assisted by heat combines with gold, and forms a very brittle alloy.

Gold is attacked neither by the alkalies nor the alkaline carbonates or nitrates.

#### COMPOUNDS OF GOLD WITH OXYGEN.

§ 1147. Two combinations of gold with oxygen are known:

1. A suboxide  $\text{Au}_2\text{O}$ ,
2. A sesquioxide  $\text{Au}_2\text{O}_3$ ,

neither of which forms salts with the oxides.

The suboxide  $\text{Au}_2\text{O}$  is obtained by decomposing the chloride  $\text{Au}_2\text{Cl}_3$  by a dilute solution of potassa, in the shape of a deep violet-coloured powder, which decomposes at about  $77^\circ$ , disengaging oxygen. The oxacids exert no action on this substance, while chlorohydric acid decomposes it, forming sesquichloride of gold  $\text{Au}_2\text{Cl}_3$ , while metallic gold is separated.

*Sesquioxide of gold* (often called *auric acid* on account of its property of combining with bases) is prepared by digesting a hot



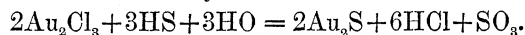
solution of sesquichloride of gold with magnesia, when aurate of magnesia is formed, which remains mixed with the free magnesia. The deposit is boiled with nitric acid, which dissolves the magnesia and leaves hydrated sesquioxide of gold. Auric acid may also be obtained by exactly saturating a solution of sesquichloride of gold by carbonate of soda, and then boiling the liquid, when a large proportion of the gold is precipitated in the state of sesquioxide, while the other portion remains in solution, but may be precipitated by successively adding to the liquid an excess of caustic potassa and acetic acid.

Hydrated auric acid is a yellow or brown powder, which loses its water at a low temperature and becomes anhydrous, while at about  $482^{\circ}$  it decomposes into gold and oxygen, which reaction is also effected by the solar light. Deoxidizing substances, such as the organic acids, or boiling alcohol, reduce it to the metallic state; while chlorohydric acid dissolves it and produces the sesquichloride  $\text{Au}_2\text{Cl}_3$ . The most energetic oxacids do not form definite compounds with sesquioxide of gold, while the latter dissolves, on the contrary, readily in cold alkaline solutions, producing alkaline aurates which crystallize by evaporation.

By adding a small quantity of ammonia to a solution of sesquichloride of gold, a fulminating substance is produced, which contains, at the same time, oxide of gold, ammonia, and chloride, and which, by digesting with an excess of ammonia, furnishes a bright brown powder of still higher detonating properties than the first, and which is a simple combination of sesquioxide of gold with ammonia  $\text{Au}_2\text{O}_3 + 2\text{NH}_3 + \text{HO}$ .

#### COMPOUNDS OF GOLD WITH SULPHUR.

§ 1148. Although sulphur does not combine directly with gold, two sulphides corresponding to the two oxides are obtained by decomposing the sesquioxide of gold by sulphydric acid, which, on being passed through a cold solution of sesquichloride of gold, yields a brownish-yellow precipitate, which is the sulphide  $\text{Au}_2\text{S}_3$ , readily soluble in the alkaline sulphides. If the solution of the chloride is boiling, a sulphide  $\text{Au}_3\text{S}$ , of a deep brown colour, is precipitated, while sulphuric and chlorohydric acids are formed:



#### COMPOUNDS OF GOLD WITH CHLORINE.

§ 1149. By dissolving gold in aqua regia a yellow solution of sesquichloride of gold  $\text{Au}_2\text{Cl}_3$  is obtained, which, when allowed to evaporate slowly in dry air, deposits yellow crystals of a compound of sesquichloride of gold and chlorohydric acid. If the solution be evaporated to drive off the excess of acid, the substance assumes a brown colour, and a deliquescent crystalline mass remains, which

dissolves readily in alcohol and in ether. Sesquichloride of gold dissolves even more rapidly in ether than in water; for, if an aqueous solution of the chloride be shaken with ether and water, the supernatant ether contains nearly all the chloride of gold in solution. The solution of sesquichloride of gold in ether was formerly used in medicine under the name of *aurum potabile*.

Sesquichloride of gold forms with several other metallic chlorides double crystallizable chlorides, in order to obtain which it is sufficient to mix and evaporate the solutions of the two chlorides. The formula of the double chloride of gold and potassium, which is deliquescent, is  $\text{KCl} + \text{Au}_2\text{Cl}_3 + 5\text{HO}$ , while the formula of that of gold and sodium is  $\text{NaCl} + \text{Au}_2\text{Cl}_3 + 4\text{HO}$ , and that of the double chloride of gold and ammonia is  $\text{NH}_3\text{HCl} + \text{Au}_2\text{Cl}_3 + 2\text{HO}$ . Compounds of chloride of gold with the chlorides of barium, calcium, manganese, iron, zinc, etc., are also known.

Subchloride of gold  $\text{Au}_2\text{Cl}$  is prepared by heating the sesquichloride of gold  $\text{Au}_2\text{Cl}_3$  to a temperature of about  $400^\circ$ , when chlorine is disengaged, while a greenish insoluble powder remains.

#### COMPOUND OF GOLD WITH CYANOGEN.

§ 1150. By adding a solution of cyanide of potassium to a concentrated hot solution of perchloride of gold, until the liquid loses its colour, a solution is obtained, which, on cooling, deposits prismatic crystals of a double cyanide of gold and potassium of the formula  $\text{KC}_y + \text{Au}_2\text{C}_y$ . The crystals, which are efflorescent and very soluble, disengage cyanogen when subjected to moderate heat; and, when treated with water, a solution is obtained, which, on cooling, deposits a double cyanide of the formula  $\text{KC}_y + \text{Au}_2\text{C}_y$ .

#### PURPLE OF CASSIUS.

§ 1151. The name of *purple of Cassius* is given to a precipitate containing gold, tin, and oxygen, which is used by painters on porcelain and glass, (§ 730,) and which is prepared in various ways. Its composition not being always uniform, chemists are not yet agreed upon its nature. It is generally obtained by pouring into a sufficiently dilute solution of sesquichloride of gold, a mixture of protochloride and bichloride of tin, the precipitate showing a beautiful purple hue when it is of small bulk, while it assumes a brown colour when more copious.

A purple of Cassius of uniform composition is prepared by dissolving 20 gm. of gold in 100 gm. of aqua regia made of 20 parts of nitric and 80 of chlorohydric acid; driving off the excess of acid by evaporation in a water-bath and dissolving the residue in 7 or 8 decilitres of water. Some pieces of tin being then placed in the liquid, a purple precipitate of the formula  $\text{Au}_2\text{O}_3, \text{SnO}_2 + \text{SnO}, \text{SnO}_2 + 4\text{HO}$  is formed, but which may also be considered as  $2\text{Au} + 3\text{SnO}_2 + 4\text{HO}$ . The substance, on being subjected to heat, evolves water alone and

VOL. II.—2 C

no oxygen, while the calcined residue presents all the characters of a mixture of metallic gold and stannic acid. But as before calcination the substance will not give off gold to mercury, it is evident that the gold did not exist in it in the metallic state.

A beautiful purple of Cassius is obtained by heating suboxide of gold  $\text{Au}_2\text{O}$  with a solution of stannate of potassa.

Lastly, purple of Cassius is obtained by fusing together in a crucible 1 part of gold,  $\frac{1}{2}$  part of tin, and 4 or 5 of silver, forming a ternary alloy, from which nitric acid extracts the silver, while the gold and tin are precipitated in combination with oxygen, and a brilliant purple is formed, the shades of which can be changed by altering the relative proportions of gold and tin.

A solution of sesquichloride of gold stains linen of a purple colour, as it also does the skin and the organic tissues generally; which colouring is probably owing to suboxide of gold, as friction does not restore a metallic lustre to the spots, although they acquire it in a short time when exposed to solar light in a bottle filled with hydrogen gas.

#### DETERMINATION OF GOLD, AND ITS SEPARATION FROM THE METALS PREVIOUSLY DESCRIBED.

§ 1152. Gold is always determined in the metallic state, and is precipitated from its solutions by means of protosulphate of iron, after having added chlorohydric acid to the liquid in order to maintain the sesquioxide of iron which forms during the reaction in solution. But it is important, in order to completely precipitate the gold, that the liquid should contain no nitric acid; in which case it must be previously evaporated with chlorohydric acid. The gold, when collected on a filter, is calcined to redness before being weighed.

§ 1153. In order to separate gold from the metals previously described, the insolubility of the metal in nitric acid is sometimes relied on, while at other times all the metals are dissolved in aqua regia, and the gold is precipitated by protosulphate of iron, or, better still, by heating the solution with a certain quantity of oxalic acid; which latter method has the advantage of not introducing a new metal into the liquid. Gold is sometimes also separated by precipitating it in the state of sulphide, by sulphydric acid gas, the sulphide leaving metallic gold after calcination.

#### METALLURGY OF GOLD.

§ 1154. Gold is almost always found in the native state, being sometimes pure, but more generally alloyed with certain quantities of silver. It occurs in three kinds of bearings:

1. In veins, generally quartziferous, which contain other metallic minerals, as ores of copper, lead, silver, and pyrites; the veins usually traversing the primitive rocks.

2. In small veins scattered through rocks situated at the separation of the crystalline and stratified rocks.

3. In disaggregated quartzose sands, often extensively seen in alluvial formations, and owing their presence to the disintegration of auriferous crystalline rocks which exist in the vicinity. The greater specific gravity of the gold prevents its particles from being carried as far as those of the other minerals with which it was mixed, and its resistance to the action of the greater part of chemical agents preserves it in the state of spangles. Alluvial soils containing gold chiefly occur in open valleys between primitive mountains, where gold is frequently found in place. The principal localities of auriferous sands are in California, Australia, Brazil, Mexico, Chili, Africa, the Ural and Altai Mountains in Siberia—the quantity of gold annually extracted from all of which amounted, in 1851, to 178 tons, of which California alone produced 110. Gold is generally found in the sands in the form of spangles, or shapeless and rounded grains, which, when they are of any considerable size, are called *river* or *wash gold*, (*pépites*.) Grains are sometimes found of the size of a hazel-nut, and pieces weighing several kilogs. have been met with: one lump weighing 36 kilogs. was found in the Ural.

Gold exists in the drift-sand of all rivers which arise from, or flow over a large extent of, primitive rocks; and several auriferous alluviae are known in France, such as those of the Ariège in the Pyrenees, of the Gardon in Cevennes, the Garonne, and the Rhine near Strasburg. It is found in too small quantity to be worked to advantage; but the inhabitants look for it when they would otherwise be idle, and are then called *gold-finders*. The spangles of gold scattered through the river-sand are generally so excessively small that more than 20 are often required to make a milligramme.

In Siberia, sands containing only 0.000001 of gold are not considered worthy of being worked; and the Rhenish sands contain, on an average, about  $\frac{1}{8}$  of this quantity.

Gold exists also, combined with tellurium, in certain mines of Transylvania. An alloy of gold with silver and palladium, in the form of small crystalline grains, occurs in Brazil, and is called *auro-powder* or *auro-dust*. Lastly, all pyrites in primitive rocks contain a small quantity of gold, and are often rich enough to be worked to advantage.

§ 1155. When gold exists in veins which contain other metals, as lead, copper, or silver, those metals in which the gold is concentrated are first extracted from the ores, and the gold is then separated by *refining*, a process presently to be described.

The ore is frequently first subjected to amalgamation, as in the case of silver ores, when the gold dissolves in the mercury, and, after the liquid amalgam has been filtered, a more solid amalgam is obtained, from which the gold is separated by distillation. The ore

is then smelted, so as to obtain a matt from which a certain quantity of gold can still be extracted.

§ 1156. Auriferous sands are washed in the most simple manner, either in wooden tubs, or on inclined planes over which a current of water flows, and they are then treated by amalgamation.

In the Ural, the auriferous sand is poured into boxes, the sheet-iron bottom of which is provided with openings of 2 centimetres in diameter, and, while a stream of water flows through the boxes, the workman stirs the sand constantly with a shovel, when the finer portions fall through the holes and are collected on large sleeping tables covered with muslin. The sand is frequently swept toward the head of the table, where the gold remains with the heavier minerals; and the sand, being enriched by this washing, is again more carefully washed on smaller tables. The titaniferous iron and magnetic oxide of iron being separated by a magnet, the material is fused in large graphite crucibles, at the bottom of which the gold collects, while the upper part is filled by a slag containing a quantity of unmelted grains of gold. The slag being stamped and washed, the rich schlich thus obtained is smelted, yielding an auriferous lead, from which the gold is separated by cupellation.

§ 1157. In Tyrol a certain quantity of gold is extracted from pyrites by amalgamating them in mills resembling that represented in fig. 601, several mills being generally placed above each other. (The figure gives an external view of the upper mill and a section of the lower one.)

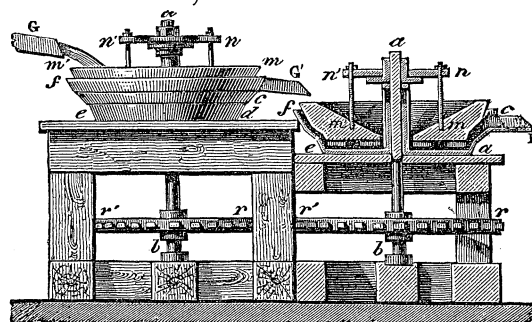


Fig. 601.

fastened on a strong wooden table; and in the centre of the vessel is a tubulure traversed by an axis of rotation *ab*, set in motion by the cog-wheel *rr'*. The runner-stone *mm'* of each mill is of wood, and resembling the shape of the bed; but, being about 2 centimetres smaller, is furnished with several sheet-iron teeth projecting about 1 centimetre. The upper surface of the runner-stone is shaped like a funnel, into which is poured the liquid mud, which passes between the stones and flows out by the conduit *G'*.

The stones make about 15 or 20 revolutions per minute; and 25

The pyrites, in the state of an impalpable powder, is suspended in water, and conveyed into the upper mill by the conduit *G*, whence it flows into the second mill by the sluice *G'*. The bed of each mill is made of a cast-iron vessel *cdef*, securely

kilogs. of mercury are placed at the bottom of each, making a layer of about 1 centimetre in thickness, against which the teeth of the wheel constantly strike, while at the same time they stir up the ore. The gold is dissolved by the mercury, and, after continuing this process for 4 weeks, it is withdrawn and filtered through a chamois-skin, which retains a solid amalgam containing nearly one-third of its weight of gold, which is then separated from the other metals by cupellation.

## ALLOYS OF GOLD.

§ 1158. Gold is rarely used in a state of purity, as it is too soft, and its hardness must be increased by the addition of a small quantity of silver or copper, forming more fusible alloys than pure gold.

The standard of French gold coin is  $\frac{900}{1000}$ , the law allowing a variation of  $\frac{2}{1000}$  above and  $\frac{2}{1000}$  below; while medals contain 0.916 per cent. of gold, with the same variation. There are three legal standards for jewelry, the most common of which is  $\frac{750}{1000}$ , while those of  $\frac{840}{1000}$  and  $\frac{920}{1000}$  are rarely used; and the legal variation is  $\frac{3}{1000}$  below the standard, no superior limit being fixed.

Gold is soldered with an alloy called *red gold*, of 5 parts of gold, and 1 of copper; an alloy made of 4 parts of gold, 1 of copper, and 1 of silver also being used.

The clear colour of gold is given to jewelry by dissolving the copper which exists in the superficial layer; to effect which the articles are heated to a dull red-heat, and dipped, after cooling, into a weak solution of nitric acid, which dissolves the copper. A thicker coating of pure gold is obtained by allowing them to remain for 15 minutes in a paste formed of saltpetre, common salt, alum, and water; the chlorine set free by the action of the sulphuric acid on the salt and saltpetre dissolving the copper, silver, and gold, while the latter metal is again deposited on the article. The surfaces are then burnished.

## SEPARATION OF GOLD AND SILVER.

§ 1159. The separation of gold and silver, more generally called the *refining of the precious metals*, is now done by treating the alloy by concentrated hot sulphuric acid, which dissolves the silver only. But, in order that the alloy may be completely acted on, it should neither contain more than 20 per cent. of gold, nor than 10 per cent. of copper, because sulphate of copper is but slightly soluble in concentrated sulphuric acid. The alloys are fused in crucibles, and when they are too rich in gold, a certain quantity of silver is added—silver containing a small quantity of gold being preferred. The fused alloy is granulated by being poured into water, and then placed in a large kettle with  $2\frac{1}{2}$  times its weight of concentrated sulphuric acid marking 66° on the areometer, the kettle being covered with a lid furnished with a disengaging tube. The acid, being

heated to boiling, is partly decomposed, and sulphates of silver and copper are formed, while sulphurous acid is disengaged, which is sometimes passed into the leaden chambers where sulphuric acid is manufactured, (§ 139.) When gold coin is to be refined, it is merely roasted.

After 4 hours, when the alloy is completely destroyed, there is introduced into the kettle a certain quantity of sulphuric acid marking  $58^{\circ}$ , and obtained by the concentration of the acid mother liquid of the sulphate of copper obtained in refining, as will presently be explained. After having boiled the liquid for fifteen minutes, the kettle is taken from the fire and allowed to rest, when the greater part of the gold collects at the bottom of the vessel, from which the nearly boiling liquid is decanted off into leaden boilers containing the mother liquid arising from the purification of the sulphate of copper by crystallization. The boilers are heated by steam; and after the sulphate of copper at first deposited is redissolved, the liquid is allowed to rest for some time, when the whole of the gold is deposited. The clear liquid is then drawn off by a siphon, and passed into other boilers heated by steam, and containing blades of copper, which precipitate the silver in the form of small crystalline grains; the metal being in a short time so perfectly precipitated that the liquid is not clouded by common salt. The precipitated silver is carefully washed, and then compressed by an hydraulic press into compact prisms, which, after being dried, are melted in earthen crucibles, furnishing a metal which contains only a few thousandths of copper.

As the gold arising from the first action of the sulphuric acid still contains a certain quantity of silver, it is heated anew, in a platinum crucible, with concentrated sulphuric acid, which abstracts the balance of the silver; a third treatment with sulphuric acid being often required. The gold dust, after being well washed and fused, contains 995 thousandths of pure gold.

The acid solution of sulphate of copper which arises from the precipitation of the silver by copper is evaporated in leaden kettles until it marks  $40^{\circ}$  on the areometer; a large proportion of the sulphate of copper being deposited in small crystals during the cooling. After another evaporation, the mother liquid yields an additional quantity of crystals; and the last liquid, which refuses to crystallize, is used as a solution of sulphuric acid, and poured into the cast-iron boiler, after this action on the alloy. The sulphate of copper is purified by recrystallization.

When the quantity of gold and silver contained in an alloy does not exceed 0.200 or 0.300, the granular material is first heated in a reverberatory furnace, when a portion of the copper is converted into oxide, which is dissolved by treating the roasted substance with weak sulphuric acid; and the alloy, being thus brought to the me-

dium standard of 0.500 or 0.600, may be refined by the ordinary process.\*

## GILDING AND SILVERING.

§ 1160. Ornamental objects of copper or bronze were formerly gilded by means of an amalgam of gold, which method has now been superseded by galvanic processes: The amalgam used in *mercurial gilding* is prepared in the following manner:—Gold-leaf is heated to a dull red-heat in a crucible, and triturated with eight times its weight of mercury, and, when the gold is dissolved, it is

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\* The process of refining gold pursued at the United States Mint, in Philadelphia, is similar to the method formerly called quartation, and consists in melting gold with silver, and then extracting the silver with pure nitric acid. The deposit of grains of native gold is first melted with borax and saltpetre, occasionally with soda to remove quartz, and being cast into a bar, is carefully weighed, accurately assayed to  $\frac{1}{1000}$  for gold, and from the assay and weight the value of the deposit calculated. Although a million of dollars may be deposited in a day, upon an arrival from California, yet such is the expedition of the assay-department, that in a few days the deposits are all paid off. As soon as the gold is assayed, each pound of it is melted with 2 pounds of pure silver, and the mixture, after stirring, poured into cold water, by which it is *granulated*, divided into small irregular fragments, presenting a large surface to the subsequent action of the acid. The granulations are then put into large porcelain jars of 50 gallons each, of which there are about 70 in use, and nitric acid poured in them. The jars being placed in leaden-lined wooden troughs, containing water, are heated by a steam coil in the water, causing the nitric acid to dissolve out the larger proportion of silver. A steam-heat is given during several hours, and the liquid allowed to repose until the following morning, when the solution of nitrate of silver is drawn off by a gold siphon, and transferred to a large vat of 1200 gallons, containing a saturated solution of common salt. Fresh acid is then added to the gold in the pots, already nearly parted, steam-heat applied again for several hours, and the whole left again to repose. On the following morning the acid liquid of one of the pots being drawn off and the fine gold removed to its filter, fresh granulations of gold and silver are introduced, and the acid liquid of the adjoining pot, containing only a small quantity of nitrate of silver poured over it. A fresh charge of granulated metal is thus first worked by the yet strong acid, which acted on the nearly fine gold of the previous charge. A charge of \$800,000 or more is easily worked off, *refined*, in two days, by  $4\frac{1}{2}$  pounds of parting acid to every pound of gold. The gold is washed thoroughly on a filter by hot water, pressed in a hydraulic press, further dried, melted with copper, and cast into bars, about 2400 ounces Troy constituting a melt. After being assayed, they are then remelted with the calculated quantities of copper or fine gold requisite to bring them to our standard of 900 thousandths fine, and cast into ingots. Upon their proving correct in the assay, usually to within  $\frac{1}{1000}$  of the standard, they are delivered to be coined. The chloride of silver, accurately precipitated with a slight excess of salt, is filtered and washed thoroughly on large filters, of 3 by 5 feet and 14 inches deep. It is then transferred to lead-lined wooden vats, reduced to metallic silver by granulated zinc, and, the excess of zinc being removed by sulphuric acid, washed, pressed in the hydraulic press, dried by heat, and remelted with a new portion of gold.

This method of parting formerly required 3 parts of silver to 1 part of gold, and the latter constituting a fourth part of the alloy, the process was termed *quartation*. We have, however, found that 2 parts silver to 1 part gold are quite sufficient; and if the metal be well granulated, the acid will not leave 10 thousandths of silver in the gold, which is sufficient to prevent the too darkening effect of copper in the coin.—*J. C. B.*



thrown into cold water, in order to prevent the formation of crystals by slow cooling. The excess of mercury being removed by pressure, a doughy amalgam remains, consisting of 2 parts of gold and 1 of mercury.

Bronze objects require several preliminary preparations. They are heated to redness and then dipped into dilute sulphuric acid to dissolve the oxide which forms on the surface, which operation is called the *cleaning*, (*dérochage*,) and they are sometimes dipped for a moment into concentrated nitric acid, in order to obtain a more perfect cleansing, called *ravivage*. The surface is then amalgamated by means of the *scratch-brush*, made of fine brass wire, which is first dipped into a solution of nitrate of mercury, and then pressed on the amalgam of gold, part of which adheres. The article, being rubbed with the brush, is placed on an iron grate over coals, in a chimney which must draw well, in order to carry off the mercurial vapours, which would injure the health of the workmen. The article is then cleaned with a brush dipped in vinegar, and the parts which are to be bright are polished with blood-stone.

By substituting an amalgam of silver for one of gold, and operating in the same manner, copper, bronze, and brass can be covered with a coating of silver. The brass scales of barometers and other instruments are silvered by being rubbed with a cork moistened with mixture of 1 part of chloride of silver, 2 of carbonate of potassa, 1 of common salt, and  $\frac{2}{3}$  of a part of chalk.

#### *Gilding by Immersion.*

§ 1161. This process, which is chiefly used for gilding copper jewelry, consists in plunging the articles, after being cleanly scraped, into a boiling solution of chloride of gold in an alkaline carbonate, which is prepared by dissolving, on the one hand, 100 grammes of gold-leaf in 250 grammes of nitric acid at  $97^{\circ}$ , 250 gm. of concentrated chlorohydric acid, and 250 of water, and on the other hand, 3 kilogs. of carbonate of potassa in 20 litres of water, heated in a cast-iron kettle. When the gold is entirely dissolved in the aqua regia, the liquid is poured into a porcelain capsule, and 3 kilogs. of bicarbonate of potassa are gradually added, when a lively effervescence ensues, after the termination of which the contents of the capsule are thrown into the kettle. The liquid is boiled for 2 hours, replacing by hot water that which evaporates; after which the gold-bath is ready for gilding.

When the copper articles are prepared for gilding, they are bound together with a brass wire and suspended to a glass hook. At the right of the bath are placed, 1st. A vessel containing a mixture of nitric, sulphuric, and chlorohydric acids; 2d. Two vessels filled with water; 3d. A vessel containing a solution of nitrate of mercury; 4th. A vessel containing water; while at the left of the bath are 2 or 3 pots holding water. The workman first dips

the articles into the acid liquid, and then, successively, into the two vessels holding water, into that of nitrate of mercury, into the succeeding one of water, and lastly, into the gold-bath. When they have remained in the bath for about 30 seconds they have taken all the gold they can receive, and are then removed, washed in the pots on the left, and dried in heated sawdust.

Their colour is then given by means of a mixture of 6 parts of nitre, 2 of sulphate of iron, and 1 of sulphate of zinc, dissolved in a small quantity of boiling water, into which the gilded articles are dipped; after which they are dried before a bright fire until the saline coating turns brown. They are then washed with water.

### *Galvanic Gilding.*

§ 1162. By means of galvanism a perfectly adherent coating of gold, of any desired thickness, may be applied to copper, brass, bronze, silver, platinum, iron, steel, etc.; and by using corresponding solutions, silver, platinum, cobalt, zinc, etc., can also be deposited on copper and its alloys. The solutions used for galvanic processes are those of cyanide of potassium in which a cyanide of the metal to be deposited has been dissolved; and the same liquid may be used *ad infinitum* if a clean blade of the metal to be precipitated be kept in the solution and placed in communication with the positive pole of the battery. As the metal in solution is deposited on the articles which communicate with the negative pole, an equivalent quantity of the metal fixed to the positive pole dissolves, while the composition of the liquid remains uniform, if the surface of the metallic blade is nearly equal to that of the objects to be covered. The best solution for gilding is made of 100 parts of distilled water, 10 parts of cyanide of potassium, and 1 part of cyanide of gold. The liquid is placed in a large wooden vat

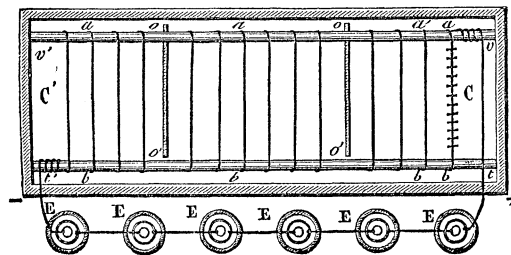


Fig. 602.

CC' (fig. 602) lined with mastic, and traversed by two gilded metallic rods  $tt'$ ,  $vv'$ , which dip into the liquid, the rod  $tt'$  communicating with the negative pole, and the rod  $vv'$  with the positive pole of the battery, while

two large sheets of gold or heavily gilded copper  $oo'$  dip into the bath and communicate with the rod  $vv'$ . Resting on the rods  $tt'$  and  $vv'$  are movable rods  $ab$ , of gilded brass, to which the objects to be gilded are suspended.

The battery is formed of plates of zinc and copper, dipping into a weak solution of sulphuric acid; each element being commonly

composed of a wooden vessel, lined with mastic, in which two concentric cylinders of copper and zinc, kept apart by wooden pegs, are arranged. The zinc cylinder has been first amalgamated with mercury, in order to protect it from too rapid solution. Water acidulated with sulphuric acid, marking  $5^{\circ}$  degrees on Baumé's areometer, being placed in the vessels, the zinc of each element is made to communicate with the copper of the succeeding one by means of a strong brass wire attached to the upper part of the cylinders, while the free zinc cylinder of one of the two extreme elements is placed in communication with the rod *vv'* which forms the positive pole, and the copper cylinder of the other extreme element communicates with the rod *tt'* which constitutes the negative pole of the battery.

The objects to be gilded should be prepared as for gilding by immersion, but the ravivage is unnecessary. The time of immersion varies with the thickness of the coat required; and the temperature of the bath should be between  $59^{\circ}$  and  $68^{\circ}$ . In order to ascertain the quantity of gold deposited, it is sufficient to weigh the object before and after immersion.

Although the solution, the composition of which was just explained, is ordinarily used, the same effect can be obtained with different materials; and either the cyanide of potassium may be replaced by the double cyanide of iron and potassium, or the cyanide of gold by its sesquioxide, or by the double chloride of gold and potassium, or, lastly, by sulphide of gold. The same process is adopted for the gilding of iron, steel, or tin; but a small quantity of copper must previously be deposited on the object by dipping it, for a few moments, in a bath composed of 1 part of cyanide of copper and 10 parts of cyanide of potassium dissolved in 100 parts of water.

#### *Galvanic Silvering.*

§ 1163. Galvanic silvering is applied chiefly to objects made of German silver, or other compositions which closely resemble silver-plate. The thickness of the coating of silver may be increased at pleasure.

The solution used for silvering is made of 100 parts of distilled water, 10 of cyanide of potassium, and 1 of cyanide of silver; the process being the same as that for gilding, with the exception that the sheets of gold in the bath (fig. 602) are necessarily replaced by sheets of silver. The silvered pieces, which, on leaving the bath are of a dead-white colour, are polished by the burnisher, and then heated to a dull red-heat in a muffle, after being dipped into a solution of borax. When cooled, they are plunged into a weak solution of sulphuric acid, and then dried.

By an analogous process, platinum may be deposited on copper or silver; but it adheres with difficulty, and, as yet, it has been found impossible to protect articles covered with platinum from the action

of nitric acid. Solutions for the deposition of zinc and lead are prepared by dissolving oxide of zinc or oxide of lead in a solution of cyanide of potassium.

## GALVANOPLASTICS.

§ 1164. By means of a feeble electrical current a uniform and firm coat of copper can be deposited on any given object, and a raised surface thus be reproduced in relief with extreme exactness. The copper plate thus produced can be used as a mould to form, by means of a galvanic current, a second deposit of metallic copper, reproducing faithfully the original object. These processes are applied to the reproduction of medals and copper plates, the battery used being the same as that employed for gilding, while the liquid for coppering consists of a slightly acidulated saturated solution of sulphate of copper, into which the object on which the metallic copper is to be precipitated is dipped, after being brought into communication with the negative pole. The positive pole terminates in a plate of copper of about the same size as the object to be coppered, and parallel to it at a short distance. In order to reproduce a medal, the first step is to make its mould in relief, either with plaster, (§ 560,) or with fusible alloy, (§ 316,) or with stearic acid, and afterward render it impervious, by immersing it, for a few moments, in a melted mixture of stearic acid and white wax, after which it is lined with plumbago, uniformly spread over it with a brush. The object of this coating is to render the surface of the mould a conductor of electricity; which being done, the mould is dipped into the solution of sulphate of copper, after having secured it by a small copper band around its circumference and fastened it to the negative wire of the battery. The copper which is deposited on the mould can be made of any thickness by keeping it for a sufficient length of time in the bath, and it separates very readily from the mould, which can be used for any number of times. The copper thus precipitated by the galvanic current is in crystalline grains, which are the smaller the more feeble the current is.

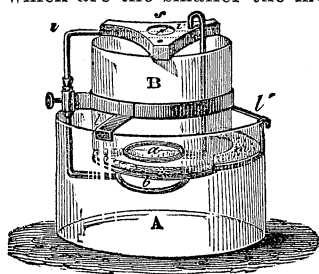


Fig. 603.

A glass cylinder B, open at both ends, is held up by the support *l, l', l''* in the vessel A; the bottom of the cylinder being made of

In order to reproduce the medal, it is not necessary to use a separate battery, as the experiment may be so arranged as to produce the galvanic current in the bath itself. Fig. 603 represents a small apparatus generally used for this purpose. A is a glass vessel, filled with a saturated solution of sulphate of copper, to maintain the saturation of which crystals of sulphate of copper are placed on the stand *m*.

some porous membranes—a bladder, for instance. A weak solution of sulphuric acid is poured into the vessel B; and two metallic rings *a*, *b*, terminating in metallic rods united at their upper part, are dipped, the one *b* into the solution of sulphate of copper, the other *a* into a solution of sulphuric acid, and are kept separated by the membrane. A plate of amalgamated zinc is placed on the ring *a*, while the mould, on which the copper is to be precipitated is set on the ring *b*; and the intensity of the electrical current is gauged by passing the upper leg, *ii'*, of the metallic rods which support the rings *a* and *b*, below a movable magnetic ring, the deviations of which are in proportion to the activity of the current.

#### ANALYSIS AND ASSAYING OF ALLOYS OF GOLD.

§ 1165. Alloys of gold and copper may be analyzed by cupelling them with lead, and following exactly the same process as described for the cupellation of alloys of silver and copper. If the alloy contains no silver, the weight of the lump obtained represents pretty exactly the quantity of pure gold which existed in the alloy; but if, as more frequently happens, the alloy contains a certain proportion of silver, this latter metal remains alloyed with the gold after the cupellation. However, the process of direct cupellation is attended with surplusses and losses which sometimes reach 3 thousandths: when the temperature of the muffle is very great, there is a small loss arising from the absorption of a small quantity of gold by the cupel; and when the heat is too low, the gold retains a small quantity of copper and lead; although gold loses less by volatilizing than silver.

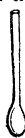
In order to determine exactly the quantity of gold existing in a ternary alloy of gold, silver, and copper, it is cupelled at a moderate heat with a certain quantity of silver and lead, in order to obtain an alloy of silver and gold, from which the latter can be perfectly separated by means of an excess of nitric acid, which dissolves the silver and leaves the gold pure. In order, however, to insure exact results, there must be a certain ratio between the quantities of gold and silver; because, if the proportion of silver be too small, the nitric acid does not dissolve it entirely; and if, on the contrary, the quantity of silver be too great, the silver and copper are completely dissolved, while the gold separates in the form of powder, which it is difficult to collect without loss. Experience has shown that the most favourable conditions for the assay, commonly called the parting, (*départ*), consist in reducing the alloy to  $\frac{1}{4}$  of gold and  $\frac{3}{4}$  of silver, in which case it is completely acted on, while the separated gold preserves the form of the original alloy, and does not become divided, if the operation be carefully conducted. This operation has received the name of *quartation*.

The proportion of lead to be added, which varies with the standard of the alloy, is indicated in the following table:—

Standard of gold alloyed with copper.	Quantity of lead necessary to be added to entirely remove the copper by cupellation.
1000 thousandths .....	1 part.
900 " .....	10 "
800 " .....	16 "
700 " .....	22 "
600 " .....	24 "
500 " .....	26 "
400 } .....	34 "
300 } " .....	
200 } .....	
100 }	

Let us suppose that the standard of a piece of coin is to be determined, the legal standard of which may be regarded as its approximate standard, is  $\frac{900}{1000}$ . The quantity of alloy usually operated on being 0.500 gm., containing, according to the legal standard, 0.450 gm. of gold, therefore 1.350 gm. of silver and 5 gm. of lead must be added. But if an alloy is to be assayed the legal standard of which is entirely unknown, the first step is to ascertain the latter by approximation, by means of the *assay by the touch-needle*, about to be described, after which the process is continued as usual.

The lead is first placed in the heated cupel, and when it is in fusion, the mixture of gold and silver is introduced, having been previously weighed and wrapped in a piece of paper. The cupellation is allowed to go on as usual, and requires less care than the cupellation of silver, because silver alloyed with gold is not liable to blister; but the cupel should be removed immediately after the lighting to avoid loss by volatilization. The lump is removed after cooling, flattened under a hammer, annealed for a few moments, and then rolled between cylinders; after which the sheet thus obtained is rolled into a spiral form, and subjected to the action of nitric acid in a small assayer's flask, (fig. 604,) into which 30 grammes of

 nitric acid of 22° Baumé are poured, and boiled for 20 minutes. The acid is then decanted and replaced by 30 gm. of pure concentrated nitric acid marking 32°, which is boiled for 10 minutes; when the acid is decanted, and the gold, which has preserved the shape of the alloy, washed several times. The flask being afterward completely filled with water, its mouth is closed with the thumb, and it is inverted, when the spiral sheet of gold falls slowly through the liquid column, and is received in a small earthen crucible, after which the water is poured off, and the crucible heated to redness in the muffle.

The acid should not be too concentrated, because the gold might be divided. When the assay has been made with the precautions indicated, the gold remains in the form of a spongy, brown, and very friable mass, of nearly the same volume as the original alloy;

but it contracts considerably when heated in the small crucible, becoming harder and assuming the lustre and colour of malleable gold. The calcined gold being exactly weighed, the standard of the alloy is thus obtained within nearly 1 thousandth.

Direct assays made on known alloys of gold and silver have shown that the operation, when carefully performed as just described, can give rise only to the following errors:—

True standards of the alloy.	Standards found.	Differences.
900 .....	900.25 .....	+0.25
800 .....	800.50 .....	+0.50
700 .....	700.00 .....	0.00
600 .....	600.00 .....	0.00
500 .....	499.50 .....	—0.50
400 .....	399.50 .....	—0.50
300 .....	299.50 .....	—0.50
200 .....	199.50 .....	—0.50
100 .....	99.50 .....	—0.50

*Assaying by the touch-needle.*

§ 1166. The assay just described cannot be applied to fine jewelry, because the article would be destroyed by the process, and gold jewelry is therefore subjected to a test called the assay by the touch-needle, which does not injure it, and yet enables a skilful assayer to determine its standard within nearly 1 thousandth. The method consists in rubbing the object against a very hard black-stone, on which it leaves marks, from the colour of which, and their behaviour when moistened with a mixture of nitric acid of a density of 1.34 with 2 per cent. of chlorohydric acid, the assayer forms an approximate opinion of the standard of the alloy. The black-stone used, called *touch-stone*, is a kind of quartz, coloured with bitumen, which formerly was imported from Lydia, but has likewise been found in Bohemia, Saxony, and Silesia. The conditions essential to a good touch-stone are: an intense black colour, incapability of being acted on by acids, hardness, and a sufficient degree of roughness to retain some of the gold.

The assayer is provided with a series of small blades, called *touch-needles*, consisting of alloys of copper and gold, the standard of each of which is exactly known, which enable him to compare the marks they leave on the touch-stone, before and after the action of the acid, with that of the alloys to be assayed.

No regard should be paid to the first marks left by the articles on the touch-stone, as they are made by the superficial layer, and always show a higher standard, because the surface consists of pure gold; and several marks should therefore be made, the last of which only is examined. Alongside of these marks others are made with that touch-needle the composition of which approaches nearest to

that of the article; when a glass rod, dipped in the acid, is drawn over both, after which the colour of each mark and the manner of action of the acid are examined.

## PLATINUM.

EQUIVALENT = 98.7 (1233.7; O = 100).

§ 1167. Platinum, which was imported into Europe only about the middle of the last century, but was long known in America by the Spanish name of *platina*, a diminutive name for silver, was for a long time quite useless, because no one could work it. The platinum of commerce is nearly pure, as it commonly contains only a small quantity of iridium, which increases its hardness, but diminishes its malleability. In order to obtain perfectly pure platinum, the metal of commerce is dissolved in aqua regia, the solution filtered, and chloride of potassium is added, which yields a copious yellow precipitate of a double chloride of platinum and potassium, very slightly soluble in water, but generally mixed with a small quantity of the corresponding double chloride of iridium and potassium. The precipitate is mixed with carbonate of potassa and heated to redness in an earthen crucible, when the chloride of platinum gives off its chlorine to the potassium of the carbonate of potassa, leaving the platinum isolated, while oxygen and carbonic acid are disengaged. The double chloride of iridium is also decomposed, but the iridium remains in the state of oxide. The calcined mass

is treated with hot water, which dissolves the alkaline salts, and the residue is acted on by weak aqua regia, which dissolves the platinum alone and leaves the oxide of iridium. Sal ammoniac is added to the solution of chloride of platinum, when a yellow crystalline precipitate of double chloride of platinum and ammonia  $\text{PtCl}_2 + \text{NH}_3, \text{HCl}$  is formed, which, on being calcined to redness after washing, leaves a spongy mass of platinum, called *platinum sponge*.

In order to reduce platinum-sponge to the state of malleable platinum, it is introduced into a brass cylinder *efgh*, (fig. 605,) the bottom of which fits into a steel cup *abcd*, while a steel piston *ijk* moves in the cylinder. When the cylinder is half-filled with platinum-sponge, the piston is introduced and struck with a hammer, at first gently, afterward more powerful; by which means a solid disk of platinum is obtained in a short time, which is heated

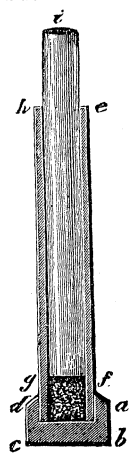


Fig. 605.



to a white-heat in a muffle, and again hammered on a steel anvil. By repeating these operations, a perfectly malleable plate of platinum is obtained, which can be rolled into sheets in a small rolling-machine.

§ 1168. Platinum resists the highest temperature of a forge-fire without fusing, but it melts before the oxyhydrogen blowpipe, or between the pieces of charcoal terminating the conductors of a powerful battery. Platinum possesses the property of being welded and soldered on itself at a white-heat, the application of which property has just been mentioned in the transformation of sponge platinum into the malleable metal.

Platinum is of a grayish-white colour, susceptible of a high polish, and possessing great malleability when pure, while the presence of a very small quantity of foreign matter will profoundly affect this quality. Although the tenacity of pure platinum is hardly inferior to that of iron, the platinum of commerce, which always contains small quantities of iridium, is much less tenacious, for a wire of 2 millimetres in diameter frequently breaks under a weight of 125 kilograms. The density of hammered or rolled platinum is 21.5.

Platinum does not oxidize in the air at any temperature, and is acted on by only a limited number of acids. Chlorohydric and concentrated sulphuric acid do not affect it, neither does nitric acid attack it, although it is soluble in this acid when alloyed with a sufficient quantity of silver. Aqua regia is the true solvent of platinum.

Platinum is acted on at a red-heat by potassa, soda, and particularly by lithia, but remains unchanged when exposed to the action of the alkaline carbonates. A mixture of nitrate of potassa and potassa acts on it much more readily than pure potassa. Sheet-platinum is acted on, only after a long time, by sulphur, phosphorus, and arsenic, while platinum-sponge combines readily with these substances, producing fusible and very brittle compounds. A mixture of silicic acid and carbon attacks platinum; in which manner platinum crucibles are frequently rendered useless. As the surface of a platinum crucible becomes rough from repeated heating, and the metal very brittle, it should never be heated in contact with charcoal, but rather be placed in earthen crucibles, at the bottom of which a small quantity of quicklime or magnesia is deposited.

§ 1169. Metallic platinum may also be obtained in the form of a very finely divided precipitate, called *platinum-black*, and then possesses remarkable properties, on which we shall dwell for a short time. Platinum-black is obtained by reducing platinum in solution by an easily combustible organic substance; to which effect a solution of chloride of platinum  $\text{PtCl}_2$  is generally boiled with carbonate of soda and sugar, when chloride of sodium is formed, while the platinum is precipitated in the metallic state and the oxygen given off by the soda decomposes a portion of the sugar into water and carbonic

acid. The flask in which the operation is performed must be frequently shaken to prevent the precipitated platinum from adhering to its sides. The precipitate is collected on a filter and dried between tissue-paper.

Platinum-black is also prepared by dissolving protochloride of platinum  $\text{PtCl}$  in a concentrated solution of potassa, boiling the liquid, and then adding a small quantity of alcohol; when a very lively effervescence of carbonic acid ensues, while the platinum is precipitated. Lastly, it is sometimes obtained by decomposing sulphate of platinum by alcohol with the assistance of heat.

Finely divided metallic platinum possesses the property of condensing gases in very large quantities. Thus, platinum-black which is allowed to remain in an atmosphere of oxygen gas will condense several hundred times its volume of the gas and afterward exhibits very intense phenomena of combustion. If, for example, a drop of absolute alcohol be thrown on platinum-black thus charged with oxygen, the whole substance becomes incandescent; and if a capsule containing platinum-black be placed under a bell-glass filled with air, the sides of which are moistened with alcohol, the vapours of the alcohol undergo a slow oxidation, which converts them into acetic acid. This property of platinum-black depends, in a great measure, on the method employed in its preparation; as for example, that obtained by decomposing sulphate of platinum by alcohol is the most active. The action may be measured in the following manner:—Having passed to the top of a graduated bell-glass filled with mercury, a small quantity of a solution of formic acid, (an organic acid which is readily converted in water and carbonic acid by oxidizing agencies,) a known weight of platinum-black wrapped in tissue-paper is introduced into the bell-glass; when the evolution of carbonic acid immediately begins, but ceases again in a few moments. By ascertaining the volume of gas disengaged, the quantity of oxygen condensed by the platinum-black can be measured.

The absorbing property of platinum black is also perceptible, though in a less degree, in platinum sponge, and even in sheet platinum. Thus, it has been shown (§ 74), that on throwing a piece of platinum-sponge into a bell-glass containing a detonating mixture of oxygen and hydrogen, an explosion immediately ensues: so again, if a current of hydrogen gas be projected on platinum-sponge exposed to the air, the jet of hydrogen ignites.

Sheet-platinum does not present these properties at the ordinary temperature, but exhibits them when heated to about  $390^{\circ}$ . If a coil of platinum wire (fig. 606) be placed over the wick of an alcohol-lamp, and the lamp lighted so as to heat the wire to redness, the wire remains incandescent for an indefinite length of time after the flame beneath has been extinguished, because the vapour of alcohol, disengaged from the wick, burning when it comes into contact

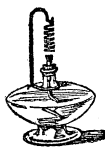


Fig. 606.

with the wire, develops heat enough to keep it incandescent. The experiment proceeds better by adding a small quantity of ether to the alcohol; and the little apparatus is known by the name of *Davy's flameless lamp*. In the same way, if a small quantity of ether be placed at the bottom of a wineglass, (fig. 607,) and a coil



Fig. 607.

of platinum wire, which has been previously heated to redness, be fastened to a pasteboard lid which closes partly the mouth of the glass, the wire remains incandescent for a long time. In these experiments, the vapours of alcohol and ether are only imperfectly burned, yielding, as products of combustion, volatile substances of highly suffocating properties and containing an organic acid; all of which shall hereafter be described.

Deutoxide of nitrogen, and ammonia, mixed with oxygen gas, are converted, by contact with platinum-sponge, into nitric acid, while the compounds of nitrogen and oxygen, on the contrary, are changed into ammonia, by contact with the sponge in an atmosphere of hydrogen. In order to succeed in the experiment, it is better to heat the platinum-sponge to a temperature of  $300^{\circ}$  or  $400^{\circ}$ , in a glass tube traversed by the gaseous mixture.

Platinum-sponge loses its absorbing property after some time, but regains it by being heated for a few moments in nitric acid, and then calcined at a dull red-heat. Platinum-black, which also loses its activity after some time, is restored to its former state by heating it with nitric acid, washing it with water, and drying it by a gentle heat.

#### COMPOUNDS OF PLATINUM WITH OXYGEN.

§ 1170. Platinum does not combine directly with oxygen, except at a red-heat, or when assisted by the caustic alkalis. Two oxides of platinum are known—

The protoxide  $\text{PtO}$ ,

The binoxide  $\text{PtO}_2$ ,

each of which is a feeble base, forming with powerful acids a series of salts which are easily decomposed by heat and leave metallic platinum.

*Protoxide of platinum*  $\text{PtO}$  is prepared by decomposing the protochloride  $\text{PtCl}$  by a solution of caustic potassa, when hydrated protoxide remains in the form of a black powder, which dissolves with a brown colour, in a concentrated solution of potassa. When heated, it first gives off its water, and then oxygen. Hydrated protoxide of platinum dissolves in acids and yields solutions of a deep brown colour, which are not precipitated by sal-ammoniac.

*Bin oxide of platinum*  $\text{PtO}_2$  is obtained by adding to nitrate of platinum one-half of the potassa which would be necessary to

completely decompose the salt, when a voluminous brown precipitate is formed, consisting of hydrated binoxide of platinum  $\text{PtO}_2 + 2\text{HO}$ . If a larger quantity of alkali were added, the precipitate would contain potassa in combination. But this oxide is more easily prepared by adding to a solution of perchloride  $\text{PtCl}_2$  a large excess of caustic potassa, when at first a yellow precipitate of double chloride of platinum and potassium is formed, but again dissolves if the liquid be heated. The platinum then exists in the solution in the state of platinate of potassa; and the liquid being supersaturated by acetic acid, hydrated oxide of platinum is precipitated. The hydrate parts with its water at a moderate heat and turns black, while it loses its oxygen when exposed to higher a temperature. It dissolves in the acids, and yields orange-yellow solutions, while after calcination it is insoluble. The hydrate also dissolves very readily in a concentrated solution of caustic potassa, and the liquid by evaporation deposits crystals of platinate of potassa. Insoluble platinate of potassa is also obtained by mixing the double chloride of platinum and potassium with a concentrated solution of potassa, drying the substance and heating it until the alkali is fused. By treating it with water the alkaline salts are dissolved, and a brown mass of platinate of potassa remains, which, when treated with acetic acid, leaves hydrated binoxide of platinum.

By adding ammonia to a solution of sulphate of platinum, a brown precipitate is obtained, which is a double basic salt, and which, on being diluted for some time with a weak solution of caustic soda, yields a substance of detonating properties when heated to about  $410^\circ$ . This fulminating compound, which, however, does not detonate by percussion, is regarded as a compound of platinum and ammonia.

#### SALTS FORMED BY THE PROTOXIDE OF PLATINUM.

§ 1171. These salts present but little interest, and have hitherto been but little studied. They form brown solutions which do not crystallize, and from which potassa does not precipitate them when sufficiently diluted, while the alkaline carbonates yield a brown precipitate, which remains suspended in the liquid. Sulphydric acid and the sulphydrates throw down a black precipitate.

The protoxalate, which is the only protosalt of platinum which has hitherto been obtained in a crystalline form, is prepared by heating the hydrated binoxide of platinum with a solution of oxalic acid, when the former is reduced to the state of protoxide, which dissolves in the excess of oxalic acid, while carbonic acid is disengaged. The liquid, when evaporated, deposits the protoxalate of platinum in small coppery-red needles.

#### SALTS FORMED OF THE BINOXIDE OF PLATINUM.

§ 1172. The salts of the binoxide of platinum are of an orange-

yellow colour, and caustic potassa throws down from their solutions a brown precipitate of the platinate of potassa, which dissolves in an excess of caustic potassa. Sulfhydic acid and the alkaline sulfhydrates yield black precipitates which dissolve in a large excess of sulfhydrate. All the salts are decomposed by heat and leave metallic platinum; and iron as well as zinc decomposes their solutions by precipitating metallic platinum in the form of a black powder. Chloride of potassium and chlorohydrate of ammonia throw down, from solutions of salts of the binoxide of platinum double chlorides,  $\text{PtCl}_2 + \text{KCl}$ ,  $\text{PtCl}_2 + \text{NH}_4\text{HCl}$ , as yellow crystalline precipitates, which are very slightly soluble in water, and nearly insoluble in a mixture of alcohol and water. The double ammoniacal chloride yields, by calcination, platinum-sponge; while the double chloride of platinum and potassium is decomposed by heat into metallic platinum and chloride of potassium; after which the substance, by treatment with water, yields pure platinum.

Bichloride of platinum is the solution extensively used in the laboratory, and presents some peculiar reactions which should be here noted. Potassa and ammonia, their carbonates, and, in general, all the salts of potassa and ammonia, precipitate platinum in the state of double chlorides, while soda and the salts of soda yield no precipitates.

*Sulphate of Bin oxide of Platinum.*

§ 1173. The sulphate of bin oxide of platinum is most easily prepared by treating the sulphide of platinum obtained by precipitating the chloride with sulfhydrate of ammonia, with fuming nitric acid, and evaporating the solution with a few drops of sulphuric acid to drive off the last particles of nitric acid; when a deep-brown mass remains which dissolves in water with a brown colour.

*Nitrate of Bin oxide of Platinum.*

§ 1174. The nitrate of bin oxide of platinum is prepared by carefully pouring nitrate of silver into a solution of bichloride of platinum until a precipitate no longer forms; when the chlorine is precipitated in the state of chloride of silver, while the solution contains nitrate of platinum, which crystallizes with difficulty. The salt may also be obtained by dissolving the hydrated bin oxide in nitric acid.

COMPOUND OF PLATINUM WITH SULPHUR.

§ 1175. Platinum combines directly with sulphur, when the metal in a very finely divided state is heated to redness in vapour of sulphur; but a purer product is obtained by heating in a crucible equal parts of ammoniacal chloride of platinum and sulphur until the chlorohydrate of ammonia and the sulphur in excess are reduced to vapour.

The sulphide thus obtained corresponds to the protoxide, and appears as a gray and very brittle mass.

The sulphide of platinum corresponding to the binoxide can only be prepared by the humid way, and is obtained by passing a current of sulphydric acid gas through a solution of the double chloride of platinum and sodium. The bisulphide is a sulphacid which enters into combination with the alkaline sulphides.

## COMPOUNDS OF PLATINUM WITH CHLORINE.

§ 1176. Two compounds of platinum with chlorine are known, corresponding to the two oxides. The *protochloride*  $\text{PtCl}$  is obtained by heating dried bichloride of platinum  $\text{PtCl}_2$  in an oil-bath, gradually raised to  $392^\circ$ , and maintained at this temperature as long as any chlorine is disengaged. The bichloride thus parts with half its chlorine and is converted into a deep-green powder, which is the protochloride of platinum. The protochloride can also be obtained in the form of a greenish-gray precipitate, by passing a current of sulphurous acid gas through a solution of bichloride of platinum which does not contain an excess of acid: sulphuric and chlorohydric acids are formed at the same time. The protochloride is insoluble in water, but dissolves in chlorohydric acid; and if sal-ammoniac or chloride of potassium be added to this solution, no precipitate is formed, while, by evaporating the liquid, beautiful crystals of double chlorides, of which the formulæ are  $\text{PtCl} + \text{KCl}$  and  $\text{PtCl} + \text{NH}_3, \text{HCl}$ , are obtained.

The *bichloride of platinum* is prepared by dissolving platinum in aqua regia, evaporating the liquid at a moderate heat to drive off the excess of acid, and then treating with water. The solution of the bichloride, which is of a slightly-brownish yellow colour, becomes deeper when it contains a small quantity of protochloride of platinum. Bichloride of platinum does not crystallize, but remains after evaporation in the form of a deliquescent brown mass, readily soluble in alcohol. It combines with a great number of metallic chlorides; and the double chlorides of platinum with potassium and with ammonia present peculiar interest in chemical analysis, because they are very slightly soluble in water and insoluble in alcohol. These compounds have already been mentioned when speaking of the determination of potassium, (§ 527.) If the double chlorides be dissolved in a large quantity of hot water, and the liquid allowed to evaporate spontaneously, they crystallize in well-defined, regular octahedrons of an orange-yellow colour. It has already been mentioned that their formulæ are  $\text{PtCl}_2 + \text{KCl}$  and  $\text{PtCl}_2 + \text{NH}_3, \text{HCl}$ . Chloride of sodium forms an analogous double chloride with chloride of platinum, which is, contrary to the corresponding compounds of potassa and ammonia, very soluble in water, and even in alcohol; and the solution of which yields, by evaporation, beautiful yellow crystals of the formula  $\text{PtCl}_2 + \text{NaCl} + 6\text{H}_2\text{O}$ .

If one of these double alkaline chlorides is intimately mixed with 2 or 3 times its weight of alkaline chloride, and heated slowly in a crucible, metallic platinum is separated in the shape of brilliant crystalline lamellæ, which are easily isolated by dissolving the alkaline chloride in water.

§ 1177. If a solution of protochloride of platinum, dissolved in an excess of chlorohydric acid, be gradually poured into caustic ammonia, small green needles of the formula  $\text{PtCl}, \text{NH}_3$  are deposited, forming a substance called *ammoniacal protochloride of platinum*; the simplest way of preparing which consists in passing a current of sulphurous acid gas through a boiling solution of bichloride of platinum containing an excess of chlorohydric acid, until the liquid no longer gives a precipitate with sal-ammoniac; by which means the bichloride of platinum is reduced into protochloride. Ammonia is then added, and the solution, on cooling, deposits ammoniacal protochloride of platinum, which is remarkable for its great stability; as it is scarcely acted on by the most powerful acids, and its ammonia can be driven off only by heating it for a long time with these acids.

Ammoniacal protochloride of platinum is soluble in a hot solution of sulphate or nitrate of ammonia, and deposits small yellow crystals on cooling, which appear to be an isomeric modification of the original product. The combination is decomposed at a temperature of  $570^\circ$ , leaving metallic platinum.

§ 1178. By digesting ammoniacal protochloride of platinum for some time in a concentrated solution of ammonia, there results a yellowish-white compound, which dissolves in the hot liquid, and is subsequently deposited, on cooling, in large prismatic crystals of the formula  $\text{PtCl}, \text{N}_2\text{H}_6 + \text{HO}$ . By pouring nitrate of silver into a hot solution of this substance, the liquid after evaporation yields a white crystallized salt, of which the formula is  $(\text{PtO}, \text{N}_2\text{H}_6), \text{NO}_3$ ; and if sulphate of silver be substituted for the nitrate, the chlorine is still precipitated in the state of chloride of silver, and the evaporated liquid deposits a second crystallized salt, of which the formula is  $(\text{PtO}, \text{N}_2\text{H}_6), \text{SO}_3$ . The compound  $(\text{PtO}, \text{N}_2\text{H}_6)$  is, therefore, a true base, which forms crystallizable salts with the acids, and which may also be obtained in an isolated state by adding a solution of hydrate of baryta to the solution of the sulphate  $(\text{PtO}, \text{N}_2\text{H}_6), \text{SO}_3$  until a precipitate no longer forms; when the sulphuric acid is precipitated in the state of sulphate of baryta, while the liquid remaining exerts a powerful alkaline reaction on coloured tests, and when evaporated under the receiver of an air-pump, deposits white crystalline needles of the formula  $(\text{PtO}, \text{N}_2\text{H}_6), \text{HO}$ . This base, which we shall call *binammonia-oxide of platinum*, combines directly with acids, even with carbonic, and is powerful enough to expel ammonia from its saline compounds.

The following compounds have been obtained in a crystallized form :

Hydrated base.....	$(\text{PtO}, \text{N}_2\text{H}_6), \text{HO}.$
Sulphate.....	$(\text{PtO}, \text{N}_2\text{H}_6), \text{SO}_3.$
Nitrate.....	$(\text{PtO}, \text{N}_2\text{H}_6), \text{NO}_5.$
Neutral carbonate.....	$(\text{PtO}, \text{N}_2\text{H}_6), \text{CO}_2 + \text{HO}.$
Sesquicarbonate.....	$2(\text{PtO}, \text{N}_2\text{H}_6), 3\text{CO}_2 + \text{HO}.$
Bicarbonate.....	$(\text{PtO}, \text{N}_2\text{H}_6), 2\text{CO}_2 + \text{HO}.$
Chloride.....	$(\text{PtCl}, \text{N}_2\text{H}_6).$
Bromide.....	$(\text{PtBr}, \text{N}_2\text{H}_6).$
Iodide.....	$(\text{PtI}, \text{N}_2\text{H}_6).$

§ 1179. The base  $(\text{PtO}, \text{N}_2\text{H}_6)$  at  $110^\circ$  loses by heat one equivalent of water and one of ammonia, being converted into a new compound, insoluble in water, of which the formula is  $(\text{PtO}, \text{NH}_3)$ . This substance, which we shall call *protammonia-oxide of platinum*, possesses basic properties in a high degree, as it combines directly with the acids, and yields the following series of products :

Anhydrous base.....	$(\text{PtO}, \text{NH}_3).$
Nitrate.....	$(\text{PtO}, \text{NH}_3), \text{NO}_5.$
Sulphate.....	$(\text{PtO}, \text{NH}_3), \text{SO}_3 + \text{HO}.$
Chloride (isomeric with ammoniacal protochloride of platinum)...	$(\text{PtCl}, \text{NH}_3).$
Iodide.....	$(\text{PtI}, \text{NH}_3).$
Cyanide.....	$(\text{PtCy}, \text{NH}_3).$

Salts of the protammonia-oxide of platinum are readily converted into those of the binammonia-oxide of platinum, by dissolving them in an excess of caustic ammonia, when they take up 1 equiv. of ammonia and reproduce the salts of the binammonia-oxide of platinum. Reciprocally, salts of the binammonia-oxide of platinum are easily converted by heat in those of the protammonia-oxide of platinum by losing 1 equiv. of ammonia.

§ 1180. The two series of salts just described are not the only ones which have been obtained by means of the ammoniacal protochloride of platinum. If the chloride  $(\text{PtCl}, \text{N}_2\text{H}_6)$  of the binammonia platinic series be boiled with weak nitric acid, reddish vapours are disengaged, and, on cooling, a substance is deposited of the formula  $(\text{PtCl}, \text{N}_2\text{H}_6)\text{O}, \text{NO}_5$ , which may be regarded as the nitrate of a *third base* represented by the formula  $(\text{PtCl}, \text{N}_2\text{H}_6)\text{O}.$

If ammoniacal protochloride of platinum be boiled with a large excess of nitric acid a liquid is obtained which deposits successively, by evaporation, two crystallizable compounds, the formula of the first of which is  $(\text{PtClO}_5, \text{N}_4\text{H}_{12}), 2\text{NO}_5$ , which forms small brilliant needles, very slightly soluble in water, and deflagrating when



heated. This compound contains a *fourth base*, of which the very complex formula is  $(\text{PtClO}_5, \text{N}_4\text{H}_{12})$ . This base has been obtained in combination with carbonic, oxalic, phosphoric, and chromic acids, forming salts which crystallize readily, because they are very slightly soluble in water.

The formula of the second compound, which remains in the mother liquid, is  $(\text{PtCl}_2\text{O}_4, \text{N}_4\text{H}_{12}), 2\text{NO}_5$ , and it may be considered as the nitrate of a *fifth base*  $(\text{PtCl}_2\text{O}_4, \text{N}_4\text{H}_{12})$ .

#### COMPOUND OF PLATINUM WITH CYANOGEN.

§ 1181. By heating an intimate mixture of finely divided platinum and ferrocyanide of potassium to a dull red-heat in an earthen crucible, and then treating the mass, when cooled, with water, a solution is obtained, which first deposits crystals of undecomposed ferrocyanide of potassium, but which yields, after additional evaporation, a double cyanide of platinum and potassium. This substance, after being purified by a second crystallization, appears in the form of beautiful crystals of the formula  $\text{KC}_y + \text{PtC}_y + 3\text{HO}$ . Its solutions precipitate a great number of metallic salts, in which precipitates the potassium of the preceding compound is replaced by 1 equiv. of the metal, of which the salt effects the precipitation.

#### DETERMINATION OF PLATINUM, AND ITS SEPARATION FROM THE METALS PREVIOUSLY DESCRIBED.

§ 1182. Platinum is determined in the metallic state, or in that of dried double ammoniacal chloride. When platinum exists in a liquid in the state of bichloride, the liquid is concentrated by evaporation, and twice its volume of alcohol is added, after which chlorhydrate of ammonia is poured into the solution, to completely precipitate the platinum in the state of double chloride of platinum and ammonia. The precipitate is washed with alcohol, and dried under the receiver of an air-pump; and the weight of the platinum is subtracted from that of the double chloride, which contains 44.23 per cent. of metallic platinum. The double ammoniacal chloride may also be calcined in a covered crucible, when sal-ammoniac is disengaged, while metallic platinum remains, which is weighed. But the decomposition by heat requires great care, because it is difficult from preventing some particles of platinum from being carried off by the vapours which are disengaged. Platinum may also be precipitated in the state of double chloride of platinum and potassium, by using the same precautions as in the precipitation by sal-ammoniac; and by decomposing the double potassic chloride by heat, there is less fear of the platinum being carried off by the gases; but as the platinum remains mixed with chloride of potassium, the residue must be washed several times to dissolve the alkaline chloride.

§ 1183. In order to separate platinum from the metals previously

described, either the insolubility of metallic platinum in all acids except aqua regia and acid mixtures which can evolve chlorine, or the precipitation of platinum by sulfhydryc acid, even in acid liquids, or, lastly, its complete precipitation by chloride of potassium or chlorohydrate of ammonia, is relied on. It is, however, important to observe that platinum, when alloyed with a considerable quantity of metal soluble in nitric acid, is itself dissolved in the acid; so that only isolated platinum can be considered as insoluble in nitric acid.

## EXTRACTION OF PLATINUM.

§ 1184. Platinum occurs in the native state in alluvial sands, resembling those in which gold is found, generally in open valleys or amid serpentine rocks. The principal localities of platinum are in Colombia, Brazil, and the Ural Mountains in Siberia. It generally occurs in small grains, although pieces weighing 10 kilogs. have been met with. The platiniferous sands, by washing, ultimately yield a sand rich in platinum, but of a very complicated composition; as it contains, in addition to the platinum, the metals which constantly accompany it, namely, osmium, iridium, palladium, rhodium, and ruthenium; and, moreover, gold, silver, iron, and copper; and lastly, many heavy minerals, such as magnetic oxide of iron, titanite iron, chromate of iron, pyrites, etc.

When the platiniferous sand contains any considerable quantity of gold, this metal is first extracted by amalgamation; when the ore, after being purified as much as possible by mechanical means, is acted on, in glass balloons heated in a sand-bath, by aqua regia containing an excess of chlorohydric acid, a small quantity of water being added, so that as little iridium as possible, which would render the platinum brittle, may be dissolved. The aqua regia is renewed several times until the platinum is completely dissolved; and the operation must be effected in a chimney which draws well, in order to carry off the vapours which are disengaged, and which are rendered injurious by the presence of osmic acid. The solution of platinum is decanted, after having been allowed to become clear by rest, and a concentrated solution of sal-ammoniac is added, which precipitates the platinum almost entirely in the state of double chloride of platinum and ammonia. As the mother liquid still contains some platinum and some quantity of foreign metals, the latter are precipitated by blades of iron and zinc, while a black deposit is obtained, from which a certain quantity of platinum may be extracted. For this purpose, the deposit is first treated with chlorohydric acid, which dissolves the foreign metals, and the residue is then acted on by very weak aqua regia, which readily dissolves the divided platinum, without sensibly affecting the iridium; when sal-ammoniac is added, which precipitates the double chloride of platinum and ammonia.

The double chloride of platinum and ammonia is calcined at a dull red-heat, and the platinum-sponge which is thus obtained is pulverized by hand, and then diluted with water so as to form a homogeneous mud, which is passed over a sieve, the grosser particles remaining on, which are again pulverized. The workman must observe the greatest cleanliness in the various operations, as the presence of dust, or even a single hair in the mud, will give rise to serious defects in the forged platinum. The powdered platinum is, therefore, generally washed several times, in order to remove all the dust.

The platinum paste is introduced into an apparatus resembling that of fig. 605, only larger, care being taken that no bubbles of air are inclosed. The substance is first compressed with a wooden pestle, then with a metallic piston; when the water separates from the platinum, while the latter becomes more solid; and the process is terminated by compressing it with great force. The platinum disc is then heated to whiteness in an earthen crucible, placed on an anvil and struck with a heavy hammer, after which it is again heated to whiteness before being forged.

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## OSMIUM.

EQUIVALENT = 99.6 (1245.9; O=100).

§ 1185. Osmium, prepared by calcining the double chloride of osmium and ammonia, is of a metallic-gray colour, resembling platinum, while, when it has been reduced by the humid way, it often shows a bluish fringe. The metal is sufficiently malleable to allow of its being rolled into plates or sheets, although it is reduced to powder by percussion. Osmium neither fuses nor volatilizes in a forge-fire, and its density is about 10. The metal combines readily with oxygen; and when it has been reduced by the humid way, it rapidly absorbs the oxygen of the air, especially when assisted by water, and is converted into osmic acid; and when heated in oxygen at a low temperature, it ignites and is converted into osmic acid, which sublimes. Concentrated nitric acid acts readily on it and disengages copious reddish vapours, producing soluble osmic acid, which product is also obtained by the action of aqua regia on the metal. The caustic alkalies and alkaline nitrates attack it at a red-heat, the osmic acid combining with the alkalies. Powdered osmium, heated on a blade of platinum, in the flame of an alcohol-lamp, disengages vapours of osmic acid, the characteristic penetrating odour of which evinces the presence of very small quantities of osmium.

## COMPOUNDS OF OSMIUM WITH OXYGEN.

§ 1186. Osmium forms a large number of compounds with oxygen, five of which are known, and are

The protoxide.....	OsO.
“ sesquioxide .....	Os <sub>2</sub> O <sub>3</sub> .
“ binoxide .....	OsO <sub>2</sub> .
“ osmious acid.....	OsO <sub>3</sub> .
“ osmic acid.....	OsO <sub>4</sub> .

The two acid compounds are the most important, and the best understood.

*Protoxide of osmium* OsO is prepared by pouring potassa into a solution of the double protochloride of osmium and potassium, when a deep-green precipitate is formed, which dissolves with a green colour in acids, and which is easily reduced to the metallic state by deoxidizing agencies.

*Sesquioxide of osmium* Os<sub>2</sub>O<sub>3</sub> is obtained by maintaining, for some time, at a temperature of 122°, a mixture of osmic acid and ammonia, when a precipitate is formed which is a compound of the sesquioxide of osmium and ammonia, and which dissolves in acids, producing yellow solutions which do not crystallize.

If chlorine be passed over a mixture of divided osmium and chloride of potassium, gently heated in a glass tube, a double chloride is obtained, of which the formula is OsCl + KCl, and which when treated while hot by a solution of carbonate of potassa, yields a black precipitate of *binoxide of osmium* OsO<sub>2</sub>.

*Osmic acid* OsO<sub>4</sub> is formed in many ways:—1. By the roasting of osmium in the air, or better still, in an atmosphere of oxygen; 2. By acting on osmium by nitric acid; 3. By heating to redness metallic osmium with nitrate of potassa, and decomposing the osmate of potassa by an acid.

Osmic acid is a white substance, which crystallizes in brilliant prisms, and exhales a very penetrating odour resembling that of chloride of sulphur; and as its vapour excites coughing and irritates the eyes and skin, the substance should be avoided with great care. Osmic acid liquifies at a temperature below 212°, and boils below a red-heat. It is very soluble in water, although the sublimed acid requires a long time for solution; and it also dissolves largely in alcohol and in ether, but after some time is reduced by these liquids, especially under the influence of polar light. It is readily decomposed by deoxidizing agencies, and by the majority of organic substances: it stains the skin and linen black. Iron, zinc, tin, copper, &c. precipitate metallic osmium from its solutions.

Osmic acid is a weak acid, which does not directly redden the tincture of litmus, and does not decompose the carbonates, but which combines with the alkalies, although the resulting compounds

are not very fixed, as solutions of the alkaline osmiates disengage, when boiled, vapours of osmic acid.

*Osmious acid*  $\text{OsO}_3$  only exists in combination with alkaline bases, and by endeavouring to isolate it, it is decomposed into osmic acid and binoxide of osmium.

Osmite of potassa is obtained by pouring a few drops of alcohol into a solution of osmiate of potassa, when the salt is deposited as a rose-coloured crystalline powder, in which case the osmic acid imparts a portion of its oxygen to the alcohol. Large crystals of osmite of potassa are obtained by allowing a solution which contains, at the same time, osmiate and nitrite of potassa to rest; when the osmic is slowly decomposed by the nitrous acid, causing beautiful crystals of osmite of potassa to be deposited.

Osmite of soda, which is prepared in the same way, and yields rose-coloured solutions, crystallizes with much difficulty, because it is more soluble.

No osmite of ammonia is known, and ammonia immediately reduces the solutions of osmite of potassa and osmite of soda.

We shall not treat of the salts formed by the oxides of osmium with acids, as they are, as yet, but little understood.

#### COMPOUNDS OF OSMIUM WITH CHLORINE.

§ 1187. If osmium be heated in a current of chlorine, two chlorides are produced: a bichloride  $\text{OsCl}_2$  and a protochloride  $\text{OsCl}$ , the latter, which is the more volatile, condensing in the most remote portions of the tube. It is an orange-coloured, very fusible and deliquescent substance, while the protochloride is of a beautiful green, and its solution in water soon decomposes, chlorohydric and osmic acids being formed, while metallic osmium is precipitated.

#### EXTRACTION OF OSMIUM.

§ 1188. Osmium always accompanies platinum-ore, but exists in it chiefly in combination with iridium, forming compounds of very variable proportions, called iridosmiums. Iridosmium is found in small, gray, very dense spangles, sometimes presenting the form of lamellæ with six facets of the rhombohedric system. Being acted on with difficulty by aqua regia, it remains in the residue after the treatment of platinum-ores. Osmium and iridium are prepared by heating in an earthen crucible, for an hour, at a strong red-heat, 100 parts of pulverized iridosmium and 300 parts of nitre, when osmiate and iridiate of potassa are formed. The fused material being run on a cold metallic plate, is then broken to pieces, and introduced into a tubulated retort, with a large excess of nitric acid, a well-cooled receiver being fitted to the retort as soon as heat is applied. A great proportion of the osmic acid volatilizes, and condenses on the sides of the receiver, in the form of beautiful white crystals, which are subsequently dissolved in a concentrated solu-

tion of potassa, from which all the osmium is afterward precipitated by alcohol, in the state of osmite of potassa, which salt is used in preparing metallic osmium and all its products.

When the substances heated in the retort no longer disengage osmic acid, water is added, and the insoluble residue being collected on a filter, then contains a certain quantity of oxide of osmium and a large quantity of oxide of iridium. It is boiled with aqua regia, which dissolves the osmium and iridium in the state of chlorides, after which sal-ammoniac is poured into the solution, when the double chloride of osmium and ammonia is precipitated, together with the corresponding compound of iridium and ammonia  $\text{IrCl}_2 + \text{NH}_3\text{HCl}$ . The double chlorides are suspended in water and subjected to the action of a current of sulphurous acid, when the double chloride of iridium  $\text{IrCl}_2 + \text{NH}_3\text{HCl}$  is transformed into the double chloride  $\text{IrCl} + \text{NH}_3\text{HCl}$  which dissolves, while the double chloride of osmium remains unchanged and is precipitated. The latter yields metallic osmium by calcination, while the solution which contains the double chloride of iridium and ammonia deposits, by evaporation, beautiful brown crystals, which yield iridium when calcined.

## IRIDIUM.

EQUIVALENT = 99.0 (1237.5; O = 100).

§ 1189. Iridium prepared by the calcination of the double ammoniacal chloride (§ 1188) presents the appearance of a gray spongy mass, resembling platinum. Iridium is difficult to solder, and hitherto has not been obtained in a malleable state; while it is still more difficult of fusion than platinum. The metal is obtained in a compact mass, very hard, and capable of a fine polish by moistening powdered iridium with water, compressing it, at first slightly between tissue-paper, and then powerfully by means of a press, and calcining it at a strong white-heat in a forge-fire. The metal thus obtained is very porous, and its specific gravity does not exceed 16.0, while the density of compact iridium is probably equal to that of platinum; as a native alloy of iridium and platinum is found, containing 20 per cent. of platinum, and crystallized in regular octohedrons, the density of which is 22.3. Nitric acid and even aqua regia do not attack iridium when isolated, although aqua regia dissolves it when alloyed with platinum or other metals. Heated to redness with potassa or nitre, iridium oxidizes, and iridiate of potassa is formed. It is attacked by chlorine at a red-heat and in the presence of chloride of potassium, a double chloride of iridium and potassium being formed.

## COMPOUNDS OF IRIDIUM WITH OXYGEN.

§ 1190. Four compounds of iridium with oxygen are known :

The protoxide.....	$\text{Ir}_2\text{O}$ .
“ sesquioxide .....	$\text{Ir}_2\text{O}_3$ .
“ binoxide.....	$\text{IrO}_2$ .
“ trinoxide .....	$\text{IrO}_3$ .

The *protoxide of iridium* is obtained by precipitating by an alkaline carbonate the double protochloride of iridium and potassium, when a greenish-gray precipitate is formed which dissolves in acids, yielding green solutions. The oxide is undecomposable by heat, but is easily reduced by hydrogen at a red-heat.

*Sesquioxide of iridium* is formed when iridium is attacked by the alkalis or alkaline metals, and appears as a black powder, insoluble in acids, but combining with the alkalis, producing brown solutions. Heat restores this oxide to the state of protoxide.

If the sesquioxide be dissolved in a solution of potassa, and the liquid be afterward saturated by an acid, a precipitate is thrown down, which turns blue by absorbing the oxygen of the air, and at last assumes an indigo colour, when it has passed into the state of hydrated *binoxide of iridium*  $\text{IrO}_2 + 2\text{HO}$ . The binoxide may also be obtained by pouring potassa into a solution of sesquichloride of iridium, when no precipitate is formed at first, while the liquid, on being exposed to the air, deposits ultimately a deep-blue precipitate.

Lastly, when the trichloride of iridium  $\text{IrCl}_3$  is precipitated by an alkali, there results a greenish-yellow precipitate of *trinoxide of iridium*  $\text{IrO}_3$ , which, however, is always combined with a certain quantity of alkali.

If an oxide of iridium be digested with a solution of formic acid until carbonic acid is no longer disengaged, a very finely divided black powder of iridium is obtained, which exerts a powerful absorbent action on gases, and causes the ignition of an explosive mixture of hydrogen and oxygen.

## COMPOUNDS OF IRIDIUM WITH CHLORINE.

§ 1191. Four chlorides of iridium, corresponding to the four oxides, are known.

*Protochloride of iridium*, which is obtained by heating to a dull-red very finely divided iridium in a current of chlorine, combines with the alkaline chlorides and with chlorohydrate of ammonia, yielding products which readily crystallize. Iridium is acted on more powerfully by chlorine when previously mixed with chloride of potassium.

*Sesquichloride of iridium*  $\text{Ir}_2\text{Cl}_3$  is prepared by dissolving the sesquioxide in chlorohydric acid, and appears as a hard, uncrystallizable, and deliquescent substance, which forms soluble double

chlorides with the alkaline chlorides and with chlorohydrate of ammonia. When solutions of these double chlorides are boiled, they deposit very slightly soluble double chlorides, which contain bichloride of iridium  $\text{IrCl}_2$ , while corresponding double compounds, containing protochloride of iridium  $\text{IrCl}$ , remain in the liquid. Sulphurous acid converts them into double chlorides containing the protochloride.

*Bichloride of iridium* is formed when finely divided iridium or its oxides are dissolved in aqua regia and heated to the boiling point, when solutions of a reddish-yellow colour are obtained. If chloride of potassium be poured into the liquid, a double chloride is obtained, the solution of which is red and deposits octohedric crystals, which are of such an intense red colour as to be nearly black, and the formula of which is  $\text{IrCl}_2 + \text{KCl} + \text{HO}$ . The ammoniacal bichloride of iridium is very slightly soluble in cold water, but forms with boiling water a solution which on cooling deposits octohedral crystals of a deep-red colour. The colouring power of this compound is very great, as 1 part will sensibly colour 40,000 parts of water; and it is a small quantity of this double chloride which often gives a red hue to the double chloride of platinum and ammonia.

Sulphurous acid converts these double compounds into soluble double chlorides, containing protochloride of iridium  $\text{IrCl}$ , and which are much more soluble, (§ 1188.)

Lastly, if an oxide or chloride of iridium be treated with concentrated aqua regia not exceeding the temperature of  $110^\circ$  or  $120^\circ$ , a deep-brown solution is obtained, which contains *trichloride of iridium*  $\text{IrCl}_3$ . This chloride does not crystallize, but also forms double chlorides with the alkaline chlorides.

The solutions of iridium and its different oxides are variously coloured, from which property the name of *iridium* has been derived.

#### COMPOUNDS OF IRIDIUM WITH SULPHUR.

§ 1192. Iridium combines directly with sulphur when the finely divided metal is heated in a current of vapour of sulphur, but it is difficult to thus obtain a perfect sulphuration of the metal. If sulphydric acid gas be passed through solutions of the various chlorides of iridium, brown precipitates are obtained which are sulphides corresponding to the chlorides. The most sulphuretted compounds act the part of sulphacids with regard to the alkaline sulphides. The affinity of iridium for sulphur is sometimes applied to the preparation of the metal, iridosmium being fused with a mixture of carbonate of soda and sulphur, when the material is acted on, and sulphides of iridium and osmium are formed, which are separated by means of water. The sulphides are easily attacked by chlorine, and yield chlorides which are isolated by the processes detailed in § 1188.



## PALLADIUM.

EQUIVALENT = 53.3 (665.2; O = 100).

§ 1193. Palladium is a brilliant metal, of the specific gravity 11.8, and of a white colour intermediate between silver and platinum, and which begins to fuse at the highest temperature of a forge-fire, and melts readily before the flame of the oxyhydrogen blowpipe. It can be soldered and forged at a white-heat, and it is malleable and readily worked into thin sheets and wire.

Palladium does not combine directly with oxygen, but it oxidizes when fused with potassa, or better still, with nitrate of potassa. Sulphuric acid does not act upon it, while nitric acid easily dissolves it when assisted by heat, and aqua regia dissolves it rapidly. It combines directly with chlorine, sulphur, and silver.

Palladium has within the last few years been brought into commerce, being obtained as an accessory product in the treatment of certain gold-ores and the gold-dust of Brazil, (§ 1154,) which consist chiefly of an alloy of gold and palladium. Palladium alloyed with  $\frac{1}{10}$  of silver is used by dentists, and it has been proposed to use it for the construction of the graduated scales of astronomical instruments, because, while it is nearly as white as silver, it is not blackened by sulphhydric acid; and the divisions on one of the largest instruments in the Paris observatory are drawn on palladium.

## COMPOUNDS OF PALLADIUM WITH OXYGEN.

§ 1194. Two combinations of palladium with oxygen are known: a protoxide  $\text{PdO}$ , and a binoxide  $\text{PdO}_2$ .

Anhydrous *protoxide of palladium* is obtained by decomposing nitrate of palladium by gentle heat, when a deep-gray, metallic powder remains, which loses all its oxygen at a higher temperature. By pouring an alkaline carbonate into a solution of protonitrate of palladium, a deep-brown precipitate of hydrated protoxide results, which readily dissolves in dilute acids.

*Binoxide of palladium* has not yet been obtained in an isolated form, and when caustic potassa or carbonate of potassa is added to a solution of bichloride of palladium, the brown precipitate which forms always contains alkali. Binoxide of palladium readily parts with half its oxygen at a slightly elevated temperature, and is completely reduced at a higher degree of heat.

## SALTS FORMED BY THE PROTOXIDE OF PALLADIUM.

§ 1195. The protosalts of palladium yield solutions of a reddish-brown colour, from which potassa throws down a brown precipitate

which dissolves in an excess of alkali, while sulphydric acid and the alkaline sulphides give black precipitates which do not dissolve in an excess of sulphhydrate. Cyanide of mercury yields a white, slightly grayish precipitate of cyanide of palladium; and iron or zinc precipitate palladium in the form of a black powder, which assumes a metallic lustre when burnished.

*Nitrate of palladium* is obtained by dissolving palladium in nitric acid, but the evaporated liquid does not deposit crystals, although, if ammonia be added, a crystallizable double nitrate is formed.

#### COMPOUNDS OF PALLADIUM WITH CHLORINE.

§ 1196. Two chlorides of palladium, corresponding to the two oxides, are known. *Protochloride of palladium*  $\text{PdCl}$  is obtained by dissolving palladium in aqua regia, when a red solution is formed, yielding on evaporation deep-red crystals, which by the action of heat are decomposed and converted into metal. Protochloride of palladium forms double chlorides with the alkaline chlorides and chlorohydrate of ammonia. The double chlorides of potassium and ammonia are very slightly soluble in water and insoluble in alcohol; their formulæ are  $\text{PdCl} + \text{KCl}$ ,  $\text{PdCl} + \text{NH}_3 \cdot \text{HCl}$ , and they form beautiful crystals; while the double chloride of sodium, on the contrary, is deliquescent and very soluble in water. The colour of these double chlorides in small crystals is of a slightly reddish-yellow.

Protochloride of palladium is converted by the action of aqua regia and moderate heat into the *bichloride*  $\text{PdCl}_2$ , which after evaporation under an air-pump assumes the form of a brown crystalline mass. Bichloride of palladium, which is not very fixed, and the solutions of which are readily decomposed by heat, forms with chloride of potassium a double chloride of the formula  $\text{PdCl}_2 + \text{KCl}$ , which, being very slightly soluble, is precipitated in red crystalline powder, consisting of small regular octohedrons.\*

#### COMPOUND OF PALLADIUM WITH CYANOGEN.

§ 1197. Palladium has a great affinity for cyanogen, and a cyanide of palladium is obtained in the form of a slightly-grayish white precipitate, by adding a soluble cyanide to the solution of a protosalt or of protochloride of palladium, the precipitation, how-

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\* The combination of palladium with iodine deserves some notice, as it is of importance in analytical chemistry, being obtained in the determination of iodine. The iodine contained in any soluble iodide may be very exactly determined by precipitating it by means of nitrate or chloride of palladium, when a black fleecy deposit of iodide of palladium is formed, which does not completely settle down until after 24 hours, and which is insoluble in water, alcohol, and ether. It begins to lose its iodine at a temperature of  $212^\circ$ , and is entirely freed from it when heated to about  $580^\circ$ , when pure palladium remains, from the weight of which the weight of the iodine with which it was combined may be deduced.—*W. L. F.*

ever, being complete only when the liquid does not contain an excess of acid. Cyanide of palladium combines with the alkaline cyanides and with cyanohydrate of ammonia.

A hot and saturated solution of the double cyanide of palladium and potassium deposits, on cooling, small crystalline spangles of the formula  $\text{PdCy} + \text{KCy} + \text{HO}$ ; while the same solution by slow evaporation at the ordinary temperature yields larger crystals of the formula  $\text{PdCy} + \text{KCy} + 3\text{HO}$ .

#### EXTRACTION OF PALLADIUM.

§ 1198. Palladium exists in small quantities in platinum-ore, and remains in the mother liquid which is obtained when a solution of platinum-ore in aqua regia is precipitated. It has already been mentioned (§ 1184) that the metals which remain in this mother liquid are generally precipitated by a blade of iron; they are then redissolved in aqua regia, and the excess of acid being driven off by evaporation, the residue is treated with water and poured into a solution of cyanide of mercury, which produces a solution of cyanide of palladium, which by the application of heat leaves metallic palladium. The greater proportion of palladium is obtained from the Brazil gold-dust, which is dissolved in aqua regia saturated with potassa, and then treated with a solution of cyanide of mercury, which precipitates the palladium alone. Palladium-sponge is converted into malleable metal by the same process as that described for platinum.

#### RHODIUM.

EQUIVALENT = 52.2 (652.5; O = 100).

§ 1199. Rhodium exists in small quantities in the majority of platinum-ores, and has also been found in America combined with gold. It is extracted from the metallic precipitate which is obtained by decomposing by a blade of iron the mother liquid which remains after the precipitation of the solutions of platinum-ore in aqua regia by sal-ammoniac. These metals being dissolved in aqua regia, the palladium is precipitated by cyanide of mercury, and the liquid is evaporated to dryness, after having added common salt and an excess of chlorohydric acid; when the excess of cyanide of mercury is converted into chloride of mercury, while double chlorides are formed with the chloride of sodium. The substance, when dried, is treated with alcohol, which dissolves the double chloride of platinum and sodium as well as that of iridium and sodium; the double chloride of rhodium and sodium, which is insoluble in alcohol, alone

remaining. This compound, after being purified by crystallization, is heated in a glass tube in a current of hydrogen, when metallic rhodium remains on dissolving the substance in water.

Rhodium has been thus called on account of the rose colour of its solutions. It is a gray metal of the specific gravity 10.6, resembling platinum, but more difficult to solder and fuse than this latter metal.

Rhodium does not oxidize in the air at the ordinary temperature, but when very finely divided readily combines with oxygen at a red-heat. The most powerful oxidizing acids, even aqua regia, do not act on the metal when pure, but it readily dissolves in aqua regia when alloyed with platinum or other metals. Potassa and nitre act on it at a red-heat, and convert it into the sesquioxide; and bisulphate of potassa also attacks it at a red-heat, forming a double sulphate of potassa and sesquioxide of rhodium.

#### COMPOUNDS OF RHODIUM WITH OXYGEN.

§ 1200. The existence of two oxides of rhodium, the protoxide  $\text{RhO}$  and the sesquioxide  $\text{Rh}_2\text{O}_3$ , is admitted.

The *protoxide*  $\text{RhO}$  is formed when very finely divided rhodium is roasted in the air at a high temperature; while if the temperature be lower, oxides intermediate between the protoxide and sesquioxide are obtained.

The *sesquioxide*  $\text{Rh}_2\text{O}_3$  is produced when powdered rhodium is attacked by a mixture of nitre and potassa, when, after treating the substance with water and washing the residue with a weak acid, the sesquioxide remains in the form of a black powder. This is the most important oxide of rhodium, as it combines with the acids and forms salts of which the solutions are red when concentrated, and rose-coloured when more diluted. Potassa precipitates the hydrated sesquioxide from its solutions on boiling the liquid, while ammonia throws down, when cold, a yellow precipitate, which is not deposited for some time, and which is a compound of the sesquioxide with ammonia. Sulfhydric acid and sulfhydrate of ammonia give brown precipitates. Hydrogen reduces solutions of rhodium when aided by solar light, and precipitates from them metallic rhodium; and iron, zinc, and copper precipitate the metal in the form of a black powder.

#### COMPOUNDS OF RHODIUM WITH CHLORINE.

§ 1201. Two chlorides of rhodium corresponding to the two oxides are known, and are prepared by treating the mixture of oxides obtained by roasting rhodium in the air with chlorohydric acid, when two chlorides are formed: the protochloride  $\text{RhCl}$ , which remains in the form of an insoluble reddish powder, and the sesquichloride  $\text{Rh}_2\text{Cl}_3$ , which dissolves. The sesquichloride produces brown solutions, and does not crystallize, but forms with

the alkaline chlorides crystallizable double chlorides, of a beautiful red colour, the best method of preparing which consists in heating, in a current of chlorine, a mixture of finely divided rhodium and alkaline chloride.

The double chloride of rhodium and sodium crystallizes in beautiful red crystals, of which the formula is  $\text{Rh}_2\text{Cl}_3 + 3\text{NaCl} + 18\text{HO}$ .

#### COMPOUND OF RHODIUM WITH SULPHUR.

§ 1202. Rhodium combines directly with sulphur at a red-heat, forming a sulphide which is fusible in a forge-fire. When sulphhydrate of ammonia is poured into a solution of the double chloride of rhodium and sodium, a brown precipitate of the sulphide  $\text{Rh}_2\text{S}_3$  is obtained.

### RUTHENIUM.

EQUIVALENT = 52.2 (652.5; O = 100).

§ 1203. A new metal, to which the name of *ruthenium* has been given, has been recently found in the platiniferous sands, occurring principally in iridosmium, which sometimes contains 5 or 6 per cent. of it. In its chemical properties, ruthenium closely resembles iridium, with which it was for a long time confounded. Ruthenium is extracted from iridosmium by heating to redness in a porcelain tube, traversed by a current of moist chlorine, a mixture of finely powdered iridosmium with one-half its weight of common salt. The mass, when cooled, is dissolved in water, producing a brownish-red solution, into which a few drops of ammonia are poured after having heated it to about  $120^\circ$ , when a brownish-red precipitate of sesquioxide of ruthenium, mixed with oxide of osmium, is formed. The precipitate is heated in a retort with nitric acid, to convert the oxide of osmium into osmic acid, which is driven off by boiling for a short time. The residue is calcined for one hour in a silver crucible, with a mixture of potassa and nitre, when the material is treated with water deprived of air by boiling, and allowed to rest for 12 hours in a bottle closely corked and wholly filled. The liquid, which is of an orange-yellow colour, is then decanted and saturated with nitric acid, when the sesquioxide of ruthenium is precipitated in a black velvetlike powder, which, by calcination in a current of hydrogen gas, yields metallic ruthenium.

Ruthenium is a gray metal, of the specific gravity of 8.6, resembling iridium; and it is infusible, does not consolidate at a red-heat, and is acted on with great difficulty by aqua regia.

Several oxides and corresponding chlorides of ruthenium have been obtained.

## FOURTH PART.

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### ORGANIC CHEMISTRY.

#### INTRODUCTION.

§ 1204. IN this fourth part it is intended to give a description of the substances found in organized beings, as well as the combinations derived from them by various chemical processes performed in the laboratory. The majority of organic compounds may be compared with those comprised under the head of inorganic chemistry, and, like the latter, may be *crystallized* by fusion, sublimation, or solution; and can combine either with acids, or with bases, or may be decomposed into acid and into basic elements, their compounds being subject to the laws of definite proportions in the same manner as substances belonging to mineral chemistry. In a word, they possess no peculiar character which authorizes, in a methodic classification, their separation from compounds of mineral chemistry, from which they are distinguished by their origin alone; the separation being only admitted because it facilitates the study of organic compounds, which are generally of a complex character, and the properties of which are more readily understood after the student has become familiarized with the most frequent and simple reactions of mineral chemistry.

There exists, however, in organized beings, a certain number of substances, the essential physical properties of which differ greatly from those just mentioned, and which constitute the organs of vegetables and animals. They are distinguished by their insolubility in solvents, and by the peculiar forms they assume under the influence of vitality. They undergo, in organized beings, a host of transformations, frequently without experiencing any remarkable change in their elementary composition, and thus become fitted for the various parts which they are destined to constitute in organic life. They can in no manner be made to assume a crystalline form; and whenever they are crystallized or included in compounds subjected to the ordinary laws of definite proportions and capable of crystallization, it will be found that they have been completely changed, and that the new differ very materially from the original substances, although their elementary composition is frequently identical.

We shall call these compounds *organized substances*, or *organized matter*, to distinguish them from other substances found in living beings, and often confounded with them under the general name of *organic substances* or *matter*, which should only be considered as indicating their common origin. The latter name, however, should be applied only to substances of the organic kingdom which are not also found in the mineral kingdom.

§ 1205. Some organic substances contain only carbon and hydrogen; and, while the majority of substances found in vegetables contain carbon, hydrogen, and oxygen, those forming the organs of animals consist of carbon, hydrogen, oxygen, and nitrogen. Similar quaternary compounds are found in almost all parts of vegetables, principally in the cereals, which, thence derive their property of nourishing animal life. Some organized beings also contain a greater number of simple bodies: thus, some contain sulphur, others phosphorus. Animals provided with a stony case, or shells, contain a large proportion of carbonate of lime, forming nearly the whole of their external envelop; while the bones of vertebrated animals contain a large quantity of phosphate and a small proportion of carbonate of lime. Lastly, in all animals and vegetables, salts are found, formed by the mineral bases, combined either with mineral or organic acids, and which, in many cases, appear essential to the existence and development of the organized being. The principal mineral bases found in organized beings are potassa, soda, lime, magnesia, alumina, oxides of iron and manganese; while the mineral acids are carbonic, phosphoric, sulphuric, nitric, and silicic acid. In addition to the salts formed by these substances, the chlorides of potassium, sodium, calcium, and magnesium, and more rarely their bromides and iodides, also occur. These mineral substances, with the exception of nitric acid, are found in the ashes of organized beings after their combustion.

Carbon and its compounds with oxygen may be ranked among organic substances, as they are, in most cases, extracted from them; and with still greater reason may ammonia be included among them, as it is always prepared from organic matter. We shall not, however, recur to those substances which have been considered in the preceding parts of this work.

§ 1206. The various organic compounds may be divided into—

1. Compounds which cannot be separated into several kinds of substances without evidently changing their constitution and nature, which we shall call *simple proximate principles*;
2. Compounds formed of one or two proximate principles, united in *definite proportions*;
3. Compounds formed by the union, in *indefinite proportions*, either of proximate principles, or definite compounds of these same principles.

We shall give the name of *species* to compounds of the first two

classes, while substances of the third class will be considered as *mixtures* of several species, which latter it is always possible to separate, either by mechanical means or chemical processes, without altering their nature.

The name of *proximate analysis* is given to the mechanical or chemical operations, the objects of which are to separate the species which immediately constitute organized beings; and *elementary analysis* is the operation by which the nature and proportions of the simple bodies composing these beings is determined. Elementary analysis is generally applied to species, because the knowledge of their composition furnishes one of their most distinctive characteristics.

#### PROXIMATE ANALYSIS OF ORGANIC SUBSTANCES.

§ 1207. The proximate analysis of organic substances is one of the most difficult problems of this branch of chemistry, because the great instability of organic matter, the facility with which it is altered by chemical agents, and the great diversity of its nature, do not permit the establishing of well-defined rules, such as those applied to the analysis of mineral substances.

Mechanical separation by the lens and microscope affords a means of separation which sometimes succeeds; and in some cases levigation may be used, by suspending the mixture in water, when the various insoluble species composing it are deposited, more or less rapidly, according to their varieties of density and shape.

*Neutral solvents*, that is, those which exert no chemical action on the organic species to be separated, afford the most ordinary means for the isolation of the latter; and the substances most frequently employed for the purpose are water, alcohol in various degrees of concentration, ether, and wood-spirit. As they are used sometimes cold and sometimes hot, it is important in the latter case to ascertain whether some of the organic species are not modified by the temperature at which the operation is being carried on. Soluble and insoluble organic substances constituting a mixture may be separated by means of neutral solvents, and the solutions, when slowly evaporated at a proper temperature, frequently deposit the species successively in the form of crystals, which can thus be isolated; and, although the separation is generally incompletely effected by the first crystallization, by redissolving the crystalline deposits which have successively formed in the same solvent, as before, and recrystallizing them, the species may be separated in a state of purity.

By subjecting a mixture of organic species to the successive action of various solvents, they can generally be separated into several parts, each of which is formed of a more simple mixture than the original mixture. By skilfully applying the action of neutral solvents, substances which do not even present great differences of solu-



bility in the same solvent can be separated, remarkable instances of which will be mentioned when treating of the analysis of fat substances.

Solvents which exert a chemical action on the organic species composing the mixture, but without modifying the species so that it cannot be restored to its original state, are frequently used with success; but their action must be limited, either to the decomposition of a compound species into simple species, or to simple combinations of the species with the substance of the solvent; in which case one or several of the species combine with the substance of the solvent, and form soluble compounds, the simple species of which may be separated without change. Thus, an insoluble salt, formed by an organic acid with a mineral or an organic base, may be decomposed by a solution of potassa or carbonate of potassa, so that the organic acid shall form a soluble compound with the alkalies, from which it may then be separated without change.

Acid solvents are also sometimes employed, as, for example, when an insoluble organic base is combined with an organic or mineral acid, forming an insoluble salt: by treating the substance with a weak solution of chlorohydric or sulphuric acid, the base is dissolved, and may be precipitated by supersaturating the liquid by potassa or ammonia.

The metallic salts are sometimes employed to effect double decomposition, in solutions obtained by treating organic mixtures by neutral or alkaline solvents. Thus, a great number of organic acids form insoluble salts with protoxide of lead; and by adding acetate of lead to their solutions, previously neutralized by potassa or ammonia, an insoluble salt, formed by the oxide of lead with the organic acid, is precipitated; and the precipitate, after being well washed, is suspended in water, through which a current of sulphhydric acid gas is passed, when the lead is converted into insoluble sulphide, while the organic acid separates and generally dissolves in the liquid.

Many organic substances, which do not change in the air in the presence of neutral solvents at the ordinary temperature, possess the property of absorbing oxygen rapidly when in contact with an alkaline liquid, in which case they are converted into acids which combine with the alkali; and it is therefore important, when alkaline solvents are used, to determine by a preliminary experiment whether the phenomenon just mentioned will take place; which is done by introducing a small quantity of the organic substance and the alkaline solvent into a graduated bell-glass, filled with air over mercury, and to observe whether the volume of air is lessened.

§ 1208. Certain organic species are isolated by distillation, which process requires great caution; and it is necessary to ascertain whether the product of distillation really pre-existed in the mixture, or whether it has resulted from changes effected by heat in the

original substances. Distillation or sublimation must, in many cases, be effected at a temperature below that of the boiling point of substances which volatilize under the ordinary pressure of the atmosphere, because the temperature of ebullition is often sufficiently elevated to change the other organic species which exist in the mixture. The substances are then heated in a current of steam, when the vapours of the organic volatile species, having considerable tension at the temperature of  $212^{\circ}$ , are continually carried over by the aqueous vapour, and condensed with it. By this process many of the odoriferous essential oils contained in plants are separated.

By applying distillation to organic substances, a mixture of several volatile species is frequently obtained, which are soluble in each other, and cannot be separated by the means of chemical combination. When such species are unequally volatile, a separation may be effected by subjecting them to successive distillations and dividing the products into fractions, if not absolute, at least sufficient for the study of the properties of the species. The difficulties of such a separation increase as the difference between the boiling points is smaller; and it is often more advantageous, instead of distilling the mixture under the ordinary pressure of the atmosphere, to boil it under a much weaker pressure, because, in that case, the ratio between their elastic forces becomes much less. We will endeavour to explain this by an example.

Let us suppose a mixture of alcohol and ether, in nearly equal proportions. Alcohol alone boils at  $173.3^{\circ}$ , and ether isolated at  $94.5^{\circ}$ , under the pressure of 29.922 inches; and we will admit, although the supposition is not entirely exact, that the mixture of alcohol and ether boils at  $94.5^{\circ}$ . The normal tension of the vapour of ether at this temperature is 29.922 inches, while that of alcohol is 4.055 inches, and the ratio of the two tensions is therefore 0.136. It is evident that the first portions which pass over in distillation will contain much more ether than alcohol, but that this will contain, nevertheless, a considerable proportion of the latter substance, since the ratio of the two tensions is represented by 0.136. If, on the contrary, the mixture be boiled under a pressure sufficiently feeble for the boiling point to sink down to  $32^{\circ}$ , the normal tension of alcohol at this temperature being 0.492 inches, while that of ether is 7.165 inches, the ratio between the two elastic forces is only 0.068, and consequently much more feeble than at the temperature of  $94.5^{\circ}$ . If, therefore, the retort containing the mixture be surrounded with ice, and the distillation effected by rarefying the air by means of an air-pump, the proportion of alcohol which will pass over in distillation at the same time with the ether will scarcely be one-half of that which distilled at the temperature of  $94.5^{\circ}$ ; and the proportion will be still less if the retort be surrounded by a refrigerating mixture of ice and common salt at  $14^{\circ}$ . In fact, at this temperature, the tension of the vapour of alcohol is 0.251

inches, while that of the vapour of ether is 4.468 inches; and the ratio of the two elastic forces is only 0.056.\*

We will not devote too much time to a general indication of the principal processes employed for the analysis of organic mixtures, as in the following a large number of examples will be given, which are better adapted to illustrate the methods.

#### ELEMENTARY ANALYSIS OF ORGANIC SUBSTANCES.

§ 1209. Although, in the preceding parts of this work, the greater part of the processes employed in chemistry, to determine the elementary composition of organic substances, have been already explained, we still think it necessary to add some new details, and indicate the various precautions to be observed, according to the nature and physical properties of the organic substances to be analyzed.

It has been mentioned (§ 1205) that the majority of substances extracted from the vegetable kingdom were composed only of carbon, hydrogen, and oxygen, while a certain number of vegetable species and the majority of animal substances contain nitrogen in addition; and lastly, that some organic substances contain sulphur and phosphorus. But, by subjecting organic substances to the various reactions capable of being performed in the laboratory, other substances are obtained, which are not organic substances, properly so called, because they have not been directly extracted from the organic kingdom, but the study of which presents great interest. Such substance, produced by chemical reactions, often contain elements which have not been met with in organic substances, properly so called, as, for example, chlorine, bromine, iodine, arsenic. Again, organic species which act the part of acids may form salts with mineral bases, while basic organic species form salts with the mineral acids.

\* The apparatus used for distillation under reduced pressure consists in a retort A (fig. 608) arranged in a small kettle containing ice or the refrigerating mixture.

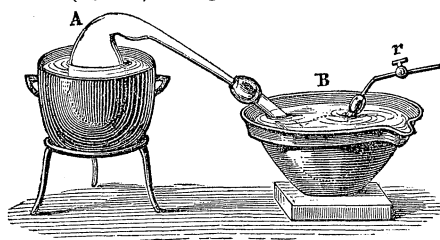


Fig. 608.

The retort is fitted to an ordinary tubulated receiver B, the corks of which are covered with sealing-wax, and which is arranged in a vessel, so that it may be entirely covered by a refrigerating mixture of crystallized chloride of calcium and ice; the temperature of which mixture must necessarily be much lower than that surrounding the retort. To the second tubulure of the receiver a leaden-pipe, having a stopcock *r* and communicating with an air-pump, is fitted. A vacuum is made until the liquid in the retort boils, when the stopcock *r* is closed, and the distillation is effected by means of the difference of temperature in the retort and the receiver. The distillation can be arrested at will, by allowing air to enter the apparatus through the stopcock *r*.

Now, the study of these salts possesses great interest, because they are more easily obtained in a state of purity than the isolated organic species, and their analysis furnishes very valuable elements for the determination of the composition and constitution of the species. From all this it will be seen that the chemist who devotes himself to the investigation of organic substances must frequently examine elements quite different from those which exist naturally in the substances subjected to analysis, and that the presence of such new elements sometimes obliges him to modify his ordinary processes.

#### DETERMINATION OF CARBON AND HYDROGEN.

§ 1210. The carbon and hydrogen of an organic compound are always determined by completely burning the substance, either in free oxygen, or by means of the oxygen contained in an easily reducible metallic oxide; when the hydrogen is converted into water, which is absorbed by some highly hygroscopic substance, such as chloride of calcium or concentrated sulphuric acid, while the carbon passes into the state of carbonic acid, which combines with a known quantity of caustic potassa; the increase of weight of the potassa representing the weight of carbonic acid formed.

Oxide of copper  $\text{CuO}$ , which is generally used to effect the combustion, may be prepared in several ways, and in each case presents some special properties on which it is proper to dwell.

One of the most simple processes consists in roasting copper turnings at a red-heat in the muffle of a cupelling furnace, (fig. 594,) when, the surface of the copper becoming oxidized, the whole is removed after a few hours' roasting, and rubbed in a mortar to detach the oxide, or to pulverize those sheets of copper which are entirely converted into oxide. The substance is passed over a coarse sieve to separate the sheets of metal, which are again roasted. A very coarse-grained oxide is thus obtained, which attracts but slightly the moisture of the air. A finer oxide, the hygrometric power of which is equally feeble, is prepared by substituting for the copper turnings, copper precipitated chemically, or produced by decomposing acetate of copper by heat.

An oxide of copper in fine powder, and more easily reducible than that prepared by roasting, may be obtained by dissolving the metal in nitric acid, evaporating the solution to dryness, and calcining for an hour, at a dull red-heat, the subnitrate of copper which remains after evaporation. The oxide, which, when ground, presents the appearance of a fine, velvet-black powder, is well adapted to the combustion of organic substances, but rapidly attracts the moisture of the air, and, on this account, requires great caution in analysis, if the amount of hydrogen is to be accurately determined.

The oxide of copper produced by the decomposition of the carbonate by heat is also well adapted to the combustion of organic

substances, but is at least as hygrometric as that prepared by calcining the nitrate; which property, however, may be lessened by heating it longer and at a higher temperature, when it again becomes more compact, and is reduced with greater difficulty by combustible substances.

Chromate of lead  $\text{PbO}, \text{CrO}_3$  is sometimes substituted for oxide of copper, because organic substances burn readily in contact with the salt; and, as the chromate fuses at quite a low temperature, the heat is raised toward the close of the combustion, so as to cause its fusion; by which means the last particles of carbon which may remain after the decomposition of the organic matter are forced into contact with the burning substance, and their combustion is necessarily complete. Chromate of lead possesses another advantage in being less hygrometric than oxide of copper, so that the determination of hydrogen may be made more accurately. The chromate of lead should be previously fused in an earthen crucible, rolled into a plate on a sheet of copper, reduced to powder, and immediately preserved in a well-stoppered bottle.

Before using oxide of copper for combustion, it is always heated to redness in an earthen crucible, in order to destroy the organic dust with which it may be mixed and drive off its moisture; and the crucible, when removed from the fire, is placed under a bell-glass containing some pieces of quicklime, and allowed to cool. It is frequently used before it is entirely cooled, as there is then less fear of its attracting moisture.

§ 1211. As organic matter burns under conditions differing slightly according to the nature of the substance, we shall pay attention to several cases.

We will suppose, in the first place, that the organic substance contains only carbon, hydrogen, and oxygen, and will also examine several points, according to the state of the substance and its greater or less volatility, assuming the substance to be solid, non-volatile, and not decomposable below  $212^\circ$ .

The combustion is effected in a glass tube  $ab$ , (fig. 609,) made


 as strong as possible, and of an internal diameter of about 15 millimetres, being  $\frac{1}{2}$  metre in

Fig. 609.

length, while one of its ends is drawn out to a point  $c$  and turned upward. The other end  $a$ , which remains open, has its edges slightly rounded, so as not to injure the cork fitted into it; which latter should be previously dried in a stove at the temperature of  $212^\circ$ , to prevent it from giving off moisture.

The glass tube intended for analysis, and which we shall call the *combustion-tube*, should be thoroughly cleaned by wiping it out with tissue-paper, and then heated throughout its whole length, while a tube open at both ends, and fitted to the nozzle of a bellows, is introduced into it, when the current of air thus established removes

all moisture; after which the tube must be closed with a cork. As the combustion-tube may still contain some organic dust, a small quantity of hot oxide of copper, recently calcined, is introduced into it, and, after having shaken the tube, the oxide is set aside.

The organic matter intended for analysis having been previously finely powdered, the portion to be subjected to combustion, which varies in weight from 8.300 gm. to 0.500 gm., is very accurately weighed. Larger quantities are sometimes taken when the substance contains but little carbon or hydrogen and great exactness is required in the analysis. It is to be weighed in a small glass tube closed at one end; and if the matter is hygroscopic, the open end of the tube should be closed with a ground-glass stopper.

The mixture of the organic matter with oxide of copper is made in a mortar of glazed porcelain or glass, which has previously been perfectly dried by being heated in a stove; but it is better to use a metallic mortar, (fig. 610,) not very deep, and highly polished on



Fig. 610.

the inside, because it is more easily heated, and because metal does not attract moisture like glass. The inside of the mortar should be cleaned, before using it, with a small quantity of oxide of copper, which is afterward rejected. The quantity of oxide of copper to be mixed with the organic matter, and which should be such as to occupy a length of 1 or 2 decimetres in the combustion-tube, being first placed in the mortar, the organic matter contained in the small tube in which it has been weighed is added; while, in order that none may adhere to its sides, a small quantity of oxide of copper is passed through the small tube several times and then poured into the mortar. The substance is ground rapidly with the pestle, in order to make a uniform mixture, which is immediately introduced into the combustion-tube, at the bottom of which a small column of pure oxide, of 3 or 4 centimetres in length, has been previously deposited; for which purpose the substance in the mortar is dipped up with the tube, or first poured on a copper spoon C,



Fig. 611.

(fig. 611,) and thence, by a copper funnel, into the combustion-tube. A small quantity of oxide of copper being rubbed in the mortar to remove any particles of the mixture which may adhere, and then dropped into the tube, the latter is then filled with pure oxide of copper.\*

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\* As Mitcherlich's old method of filling combustion-tubes, which for a long time was rejected by the majority of chemists, seems now again to be brought into use, it will be well to mention it. The organic substance is contained in a long tube, the external diameter of which is sufficiently small as to allow of its being inserted into the combustion-tube; and the oxide of copper is used, after being heated to a dull-red, while it is still of a temperature of about  $212^{\circ}$ , at which degree of heat the organic substance is supposed not to decompose. The absorption of moisture by the oxide of copper is thus prevented during the filling, which is done as follows:—Supposing the combustion-tube to be 16 inches long, the lower 2 inches would be filled with coarse oxide, and then a column of fine oxide would be in-

If the oxide of copper employed is very finely powdered, there is danger that the column will not be sufficiently porous to allow an easy disengagement of gas; and a small canal must therefore be made in the upper part of the tube throughout its whole length, which is easily effected by carefully dropping the tube lengthwise on a smooth table, and perhaps applying a few slight shocks at the ends.

As the oxide of copper during this manipulation has almost always attracted an appreciable quantity of moisture, this must be removed if the exact amount of hydrogen in the substance is to be determined; which is effected by placing the combustion-tube in a tin vessel V (fig. 612) filled with hot water, and made to communicate

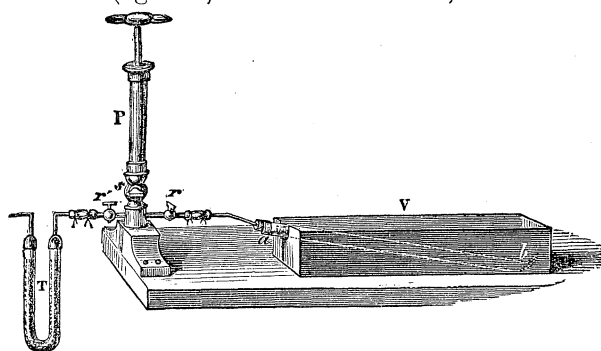


Fig. 612.

with a small air-pump P, to the second tubulure of which is fitted a tube T, filled with pumice-stone soaked in sulphuric acid. By working the pump several times, and each time

allowing the air to enter which was dried by passing through the tube T, the hygroscopic moisture is completely removed; but the process can only be employed when the organic substance does not give off sensibly any vapour, in vacuo, at a temperature of  $212^{\circ}$ , and when it cannot, under these circumstances, either give off water or decompose. In any other case the process of desiccation just mentioned could not be employed, and recourse must be taken to the use of coarser and more highly calcined oxide of copper, while

serted, occupying about 6 inches; after which the organic substance is introduced, by inserting the tube containing it in the combustion-tube, and allowing the desired quantity to fall out; after which the small tube is corked, and subsequently weighed to ascertain the amount of substance extracted. The combustion-tube is then filled with another column of 6 inches of fine oxide of copper, and the organic substance is mixed up thoroughly, by means of the spirally-twisted end of a long and clean copper wire, with the columns of oxide below and beneath it; which is easily done by successively screwing the wire down to the layer of coarse oxide, and working it backward and forward for about 5 minutes; the tube being held with a cloth, because the oxide has the temperature of boiling water. Another inch of pure fine oxide is then added, and the tube is corked. There will then be contained in the tube, 1st, two inches of coarse oxide; 2dly, twelve inches of an intimate mixture of fine oxide and the organic substance; 3dly, one inch of fine oxide; and, lastly, a free space of one inch, to allow of rendering the whole column porous by shaking.—*W. L. F.*

the mixture must be made in the mortar as rapidly as possible, taking care to hold the breath.

The combustion-tube, after being charged, is enveloped with a thin ribbon of brass, previously annealed, and fastened with copper-wire, as represented in fig. 613, after which the tube, thus protected, may be heated to a very high temperature without danger.



Fig. 613.

The combustion-tube being placed on a long sheet-iron furnace, (fig. 614,) the apparatus intended to absorb water is fitted to it by means of a very well

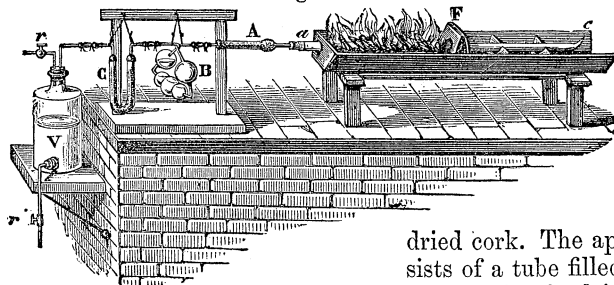


Fig. 614.



Fig. 615.

dried cork. The apparatus consists of a tube filled with pieces of chloride of calcium, arranged as in fig. 615, while plugs of cotton, placed at *a* and *b*, prevent the small particles of chloride from escaping from the tube. The cork *a* is covered with sealing-wax, in order that its weight may not change by absorbing or exhaling moisture, if any existed in the air. A U-tube, filled with pumice-stone soaked in concentrated sulphuric acid, is sometimes substituted for the tube containing chloride of calcium.

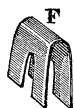
The carbonic acid formed by combustion condenses in a concentrated solution of caustic potassa, marking about 45° Baumé, and placed in the apparatus B (fig. 614) described on page 324, vol. i., which is fitted, by means of a caoutchouc connector, to a tube intended to condense the water. As it might be feared that the solution of potassa, notwithstanding its concentration, might part with a small quantity of water to the very dry gases which traverse it, a small U-shaped tube C, containing pieces of caustic potassa, which absorb at the same time the vapour of water and the small quantity of carbonic acid which escapes absorption in the apparatus B, is affixed to the latter.

Lastly, a bottle V, the cork of which has a stopcock *r*, is fitted to this apparatus, thus establishing or interrupting at will communication with the outer air. To the bottle is permanently fitted a U-tube filled with sulphuric pumice-stone, intended to prevent the vapour of water from passing from the bottle V into the tube C. (The U-tube is not represented in the figure.)



The drying-tube A and the whole of the apparatus B and C having been previously exactly weighed, their increase of weight during the experiment gives respectively the quantity of water and of carbonic acid formed by combustion.

When the apparatus is arranged, the anterior portion *a* F of the combustion-tube, which contains only pure oxide of copper, is surrounded by burning coals; and in order that the heat may not communicate by radiation to the parts of the tube containing the mixture of oxide and organic matter, a double screen F, made of



sheet-iron, and represented in fig. 616, is interposed. When the anterior portion of the tube is heated to redness, the coals are gradually moved toward the part containing the mixture of oxide and organic matter, the rapidity of moving

the coals being guided by the evolution of gas which is observed rising in bubbles through the potash apparatus, and which should never follow so rapidly as not to allow the counting the bubbles which traverse the apparatus B. This is continued until the tube is completely surrounded with coals, when the combustion is terminated, and the evolution of the gases ceases, and very soon the potassa ascends into the globe which communicates with the drying-tube, in consequence of the absorption of the carbonic acid contained in this globe. The globe apparatus is then moved from

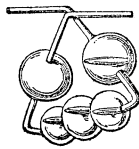


Fig. 617.

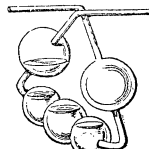


Fig. 618.

the position of fig. 617 to that of fig. 618, and if the globes are of suitable dimensions, the solution of potassa will certainly ascend to the drying-tube, (§ 260,) and very soon, the absorption of carbonic acid continuing, bubbles of air re-enter the apparatus, passing through the solution of potassa. The

coals surrounding the end *c* of the combustion-tube are then removed, and, when the latter is sufficiently cooled, its point is broken



with a pincers, (fig. 619;) when the gas in the apparatus being rarefied, the outer air enters through the broken point and establishes the equilibrium. A tube S, (fig. 620,) containing pieces of caustic potassa, and furnished with a caoutchouc tube, which it is sufficient to press against the combustion-tube to render the opening tight, is then adapted to the point; after which the stopcock *r* of the bottle V is closed, and by opening the stopcock *r'* the water in this bottle is

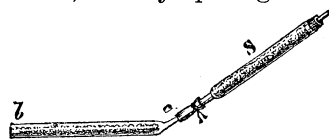


Fig. 620.

allowed slowly to escape. The atmospheric air, freed from moisture and carbonic acid by its passage through the tube S, removes the small quantities of vapour of water and carbonic acid which still remained, and conveys them into the apparatus A, B, C, where they are condensed.

When about 1 litre of water has escaped, the apparatus is taken apart, weighed, and the carbonic acid and water formed during combustion exactly ascertained, whence the quantity of carbon and hydrogen contained in the organic matter can be calculated. As we have supposed the substance subjected to analysis to contain only carbon, hydrogen, and oxygen, the oxygen may be obtained differentially, that is, by subtracting the weight of hydrogen and carbon united, from that of the substance subjected to analysis.

It frequently happens that it is difficult to completely burn organic substances, either because they cannot be intimately mixed with the oxide of copper, or because, by being decomposed by heat, they leave a charcoal of difficult combustion, which is sometimes deposited in the upper portions of the combustion-tube, out of contact of the oxide of copper. In this case, it becomes necessary to terminate the combustion in a current of oxygen; for which purpose a mixture of 2 or 3 gm. of chlorate of potassa, coarsely powdered, and 15 or 20 gm. of oxide of copper, is introduced into the bottom of the combustion-tube, while upon this is placed a column of 3 or 4 centimetres of pure oxide, then the mixture of oxide of copper and the organic substance, and lastly the tube, is filled with pure oxide. The apparatus is arranged as has been described. When the organic matter has been completely burned, and the hot coals surround the tube, even as far as the extreme portion which contains the chlorate of potassa, some coals are carefully moved toward this end, in order to disengage oxygen. The first portions of the gas are absorbed by the copper reduced by combustion, and it is only after the entire oxidation of this metal that free oxygen begins to pass through the tube, and care must be taken that its evolution be not too rapid. The organic matter is necessarily entirely burned in the atmosphere of oxygen, and the carbonic acid produced is carried by the current of oxygen into the absorbing apparatus, which renders the aspirator useless.

The chlorate of potassa should have been previously fused, in order to free it from organic substances and moisture. In this method of operating, it may be feared that the chlorate, by contact with the oxide of copper, may give off a small quantity of chlorine which is not completely retained in the combustion-tube; which difficulty, however, is remedied by using a longer combustion-tube, and placing, in front of the oxide of copper, a length of 8 or 10 centimetres of litharge, which, at a red-heat, retains the whole of the chlorine.

Sometimes the oxygen is prepared in a small separate retort, which is made to connect with the small end of the tube, instead of evolving oxygen by means of the chlorate of potassa placed in the combustion-tube itself.

Although the majority of organic substances will burn completely by contact with oxide of copper alone, it is always prudent to perform one, at least, of the combustions with the addition of chlorate

VOL. II.—2 G

of potassa, in order to ascertain whether the amount of carbon found has not been too small in the preceding analyses.

§ 1212. If the substance to be analyzed is liquid and non-volatile, as, for example, a fixed oil, it is weighed in a small tube, closed at one end, and introduced into the combustion-tube, after having poured into the latter a column of oxide of copper of 4 or 5 centimetres in height; after which the tube is inclined so as to spread the oil over a certain extent of its sides, and then entirely filled with oxide of copper. It frequently happens that complete combustion is not effected by the oxide of copper alone, and must be terminated in a current of oxygen.

Greasy and easily fusible substances should not be triturated with the oxide of copper, because some particles might adhere to the mortar and pestle; but a suitable quantity of the material should, in this case, rather be melted in a small glass boat, made of a piece of tube divided longitudinally, and introduced, after being weighed, into the tube, at the bottom of which the oxide of copper is placed. By heating that portion of the tube which contains the boat, the grease melts, and flows over a certain extent of the tube, which is then to be filled with oxide of copper. It is, in this case, equally prudent to terminate the combustion in a current of oxygen.

§ 1213. Volatile liquid substances are weighed in glass bulbs (fig. 621) hermetically sealed, the manner of making which has been described, (§ 699,) and the manner of filling them in § 269. It is essential not to bring the bubbles in contact with the hot



Fig. 621.

oxide of copper after they have been opened, as vapours affecting the accuracy of the analysis would infallibly be produced. Two tubes of nearly the same capacity are used, and one of them being filled with recently calcined and still hot oxide of copper, is closed, and allowed to cool completely; while into the second tube, which is to serve as a combustion-tube, a column of 4 or 5 centimetres of oxide of copper is introduced, and afterward the bubbles are inserted, of which one of the points is broken; and, lastly, the second tube is filled with the oxide of copper which has been allowed to cool in the first, and is, consequently, free from moisture. It is better, in such analyses, to use coarse oxide of copper, mixed with roasted turnings, because this oxide, even when it completely fills the section of the tube, is sufficiently porous to afford an easy passage for gases and vapours. The absorbing apparatus is arranged as usual, but the operation is conducted as rapidly as possible, in order that the vapours of the volatile substance may only have time to reach the anterior part of the combustion-tube, which is heated to redness, while the part containing the bubbles is protected by several screens. When the oxide of copper is red for a length of several decimetres, some coals are carefully moved toward the part containing the bubbles, while the distillation of the substance is

regulated by the position of the coals. The vapours burn while traversing the oxide of copper; and when combustion ceases, the tube is surrounded with burning coals, and heated throughout its whole length, after which the experiment is terminated as usual.

If the substance to be analyzed is very volatile—if it boils, for example, at a temperature below  $122^{\circ}$  under the ordinary pressure of the atmosphere—it is difficult to obtain an exact analysis by the process just stated. The vapours of the substance cannot be prevented from penetrating the anterior part of the combustion-tube, before this part is heated to redness, and they thus escape combustion and render the analysis inaccurate. The experiment is then arranged in the following manner:—The combustion-tube is drawn out at its posterior portion, so as to form a tubulure *c*, while the liquid to be analyzed is contained in a globe U bent into the form



Fig. 622.

of a retort (fig. 622) and terminating in two closed points, one of which enters the tubulure of a combustion-tube previously filled with oxide of copper and arranged on its sheet-iron furnace. The globe is hermetically fastened by caoutchouc, while the ordinary condensers are fitted to the combustion-tube, which is surrounded by burning coals. When the whole length of the tube is red, the anterior point of the globe is broken, by pressing it against the sides of the tubulure; and if the liquid is very volatile, it sometimes boils immediately, and the analysis may fail in consequence of a too sudden evolution of gas. If such an accident is to be feared, the globe should be surrounded by a refrigerating mixture before breaking the point; when the ebullition is easily regulated, either by heating the globe with the hand, or by hot coals. When the whole of the liquid is distilled, and the absorption of carbonic acid causes the potassa to ascend into the globe apparatus, the second point *b* of the bubble is burst, when the external air, entering the combustion-tube, carries into it the last portions of vapour which remained in the bubble. The latter is then detached, replaced by the tube *S* filled with pieces of potassa, (fig. 620,) and lastly, water is allowed to escape from the aspirator-bottle to terminate the analysis in the ordinary way.

§ 1214. We will suppose, lastly, that the organic substance to be analyzed is gaseous, and that it cannot be condensed in a refrigerating mixture at  $-20^{\circ}$ , in which case it could still be analyzed by the processes described for very volatile liquids; and the proceeding of the analysis is then as follows:

When the gas contains only carbon and hydrogen, its analysis can be very readily made. The apparatus is arranged as for the analysis of very volatile liquids, and, when the combustion-tube is heated to redness throughout its whole length, the disengaging-tube of the apparatus which produces the gas to be analyzed is fitted to its tubulure by means of caoutchouc. The gas burns when in contact

with the incandescent oxide of copper, while the vapour of water and carbonic acid are arrested in the ordinary condensers; and, when a sufficient quantity of gas is supposed to be burned, the disengagement-tube which conveys the gas is detached, and water allowed to escape from the aspirator-bottle, in order to burn the last portions of gas which remain in the combustion-tube, and drive their products into the condensers. This experiment gives the weight of carbon and hydrogen contained in the gas burned; but as the weight of this gas is not known, it is evident that only the ratio between the weight of the hydrogen and carbon can be inferred from it, which, however, will give a sufficient clue as to the composition of the gas.

It is better to operate so as to ascertain the volume of the gas

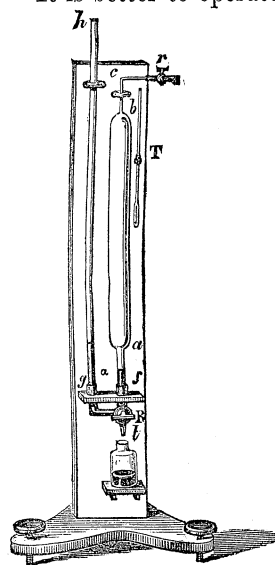


Fig. 623.

subjected to experiment, and, consequently, also its weight, if its density has been determined by previous experiment, in which case the process can also be applied to gases containing oxygen and nitrogen. For this purpose the apparatus represented in fig. 623 is used. The pipette *ab*, containing 400 or 500 cubic centimetres, terminates at its upper part, in a straight tube *cr*, to which is luted a steel tubulure, having a stopcock *r*, while the lower tube *af* of the pipette is luted to one of the tubulures of a cast-iron piece having a stopcock *R*, furnished with a second tubulure *g*. A tube *gh*, open at both ends, is luted to the tubulure *g*, and the whole apparatus is fastened to an upright board. The stopcock *R* has three apertures, as figures 624, 625, and 626 show which represent transverse sections of the stopcock, in the three principal positions which may be given to it. In fig. 624, the branches *bf* and *gh* communicate,

and in fig. 625 the branches *bf*, *gh* communicate with each other, and with the external air by the tubulure *t*, while mercury escapes; and lastly, in fig. 626 the branches do not communicate

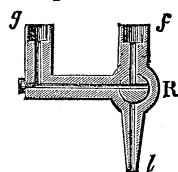


Fig. 624.

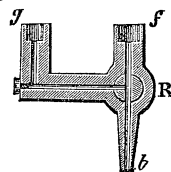


Fig. 625.

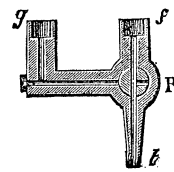


Fig. 626.

with each other, but the branch *bf* communicates with the external

air by the tubulure *t*, while the mercury contained in this branch alone escapes.

The stopcock *R* being in the position of fig. 624, and the cock *r* being open, the apparatus is filled with mercury through the tube *gh*; and when it begins to escape through the tubulure *r*, the cock *R* is brought to the position of fig. 626, and the mercury which escapes is collected in a bottle. The level of the mercury is allowed to fall until it exactly reaches the mark *a* on the tube *fa*; and the capacity of the pipette is then inferred from the weight of the mercury. The apparatus is then again filled with mercury, and the tubulure *r* made to communicate with the apparatus which disengages the gas to be analyzed. As the gas is produced, mercury is allowed to escape, so as to fill the pipette with gas to just below the mark *a*; after which the stopcock *r* is closed, the chemical apparatus which evolves the gas removed, and, bringing the cock *R* to the position of fig. 624, mercury is carefully poured into the branch *gh*, so as to bring the level exactly to *a*. By adding the difference of height *h* between the levels of mercury in the two branches *bf*, *gh*, which is then measured, to the height *H* of the mercury in the barometer, the pressure ( $H+h$ ) to which the gas is subjected is obtained, while the thermometer *T* (fig. 623) shows its temperature. If, therefore, the density of the gas be known, its weight can be easily calculated.

In order to burn the gas, it suffices to cause the tubulure *r* to communicate with the pointed tubulure *c* of the combustion-tube heated to redness (fig. 614) and furnished with its ordinary condensing apparatus. The stopcock *r* being carefully opened, mercury is poured into the branch *gh* by means of a funnel which only allows the proper quantity of mercury to escape; and as soon as the pipette is entirely filled with mercury, so that the latter reaches the stopcock *r*, this cock is closed, the apparatus of fig. 623 removed, and the operation terminated as usual.

§ 1215. In the processes just described, the weight of the carbon is inferred from that of the carbonic acid absorbed by the potassa: it may also be determined by measuring the volume of gas, by which method the first exact analyses of organic substances were made.

The hydrogen and carbon are then determined separately, the determination of the former being made in the ordinary manner, by burning the organic matter with oxide of copper, and collecting the water produced in a tube filled with pieces of chloride of calcium, and fitted to the combustion-tube by means of a cock. The determination of carbon is performed in an apparatus represented in fig. 627. The tube *ab* contains the mixture of the organic substance with oxide of copper, and at its anterior portion contains pure oxide of copper; while a bent tube *cdef*, the two vertical legs of which, *de*, *ef*, descend to the bottom of the test-glass *AB* filled with mercury, is fitted by means of a cock, to the combustion-tube, which therefore communicates with the external air by the tube *cdef*. A bell-glass *C*,

divided into cubic centimetres, and of which the sides, after being wiped with tissue-paper, retain sufficient water to saturate the air re-

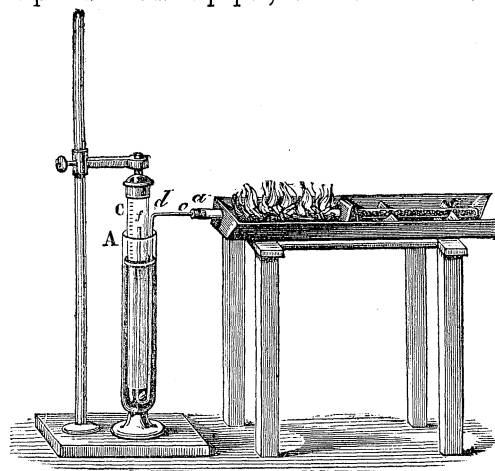


Fig. 627.

maining in the bell-glass with moisture, is passed over the leg *ef*. Before fitting the branch *c* to the combustion-tube, the bell-glass C is made to descend, until a very small volume of air (50 c. c. for example) alone remains, the mercury being on a level in the bell-glass and the circular space comprised between the bell-glass and the test-glass. The cock *c* is then fitted, and the apparatus allowed to attain the temperature of the surround-

ing medium. The temperature *t* and the height of the barometer  $H_0$  being noted down, we will designate by *v* the volume of air in the combustion-tube and in the tube *cdef*; by *f* the elastic force of the vapour of water at the temperature *t*, when the volume of air in the apparatus, supposing it to be dry, reduced to 32°, and under the pressure of 0.760 m., 29.922 inches, will be

$$(v+50) \frac{1}{1+0.00367 \cdot t} \cdot \frac{H_0-f}{760}.$$

The organic matter is then subjected to combustion; and as carbonic acid is disengaged, the bell-glass C is raised, in order to keep the surface of the mercury in the bell-glass nearly level with that in the test-glass. When the combustion is terminated, the coals are removed, and the apparatus allowed to fall to the surrounding temperature *t'*; after which the mercury inside is brought exactly to the level of that outside, by raising or depressing the bell-glass, or by pouring mercury into the test-glass. Lastly, the volume *V* occupied by the gas in the bell-glass is marked, as well as the height  $H'_0$  of the barometer. The volume of gas in the apparatus, reduced to dryness, at the temperature of 32°, and under a pressure of 0.760 m., will be—

$$(v+V) \frac{1}{1+0.00367 \cdot t'} \cdot \frac{H'_0-f'}{760};$$

and the volume of carbonic acid formed by combustion, when dry and under normal conditions of pressure and temperature, is therefore

$$(v+V) \frac{1}{1+0.00367 \cdot t'} \cdot \frac{H'_0-f'}{760} - (v+50) \frac{1}{1+0.00367 \cdot t} \cdot \frac{H_0-f}{760}.$$

In order to obtain the weight of carbonic acid furnished by the organic matter, it is sufficient to multiply this volume, in cubic centimetres, by the weight 0.0019774 m. of 1 cubic centimetre of carbonic acid.

The determination of carbonic acid by volume is much more delicate than that by weight. It is essential that the shape of the combustion-tube should not be altered during the combustion, as this would change the volume  $v$ ; and the volume of gas at the close of the experiment must not be measured until the combustion-tube attains the surrounding temperature, which often requires a long time. Lastly, it is necessary to use very coarse oxide of copper, for finely divided and feebly calcined oxide absorbs carbonic acid, in the presence of moisture, when it falls to the ordinary temperature. All these difficulties have caused this method of analysis to be neglected, although its results are accurate in the hands of a skilful manipulator.

§ 1216. When the organic substance contains, at the same time, carbon, hydrogen, oxygen, and nitrogen, the determination of carbon and hydrogen requires peculiar care. A portion of the nitrogen which is set free during the combustion of the substance by the oxide of copper, does not affect the results of the analysis, while another portion is converted into deutoxide, which, being changed into nitrous gas by contact with the oxygen of the air, condenses partly in the tube which absorbs the water, and partly in the potassa, rendering the analysis inaccurate. This is avoided by placing near the orifice of the combustion-tube a column of metallic copper of about 2 decimetres in length; when the gases which arise from combustion traversing the incandescent copper, before reaching the absorbing tubes, the oxides of nitrogen are decomposed by giving off free nitrogen, while the carbonic acid and water undergo no change. The metallic copper used to decompose the oxide of nitrogen is prepared by roasting copper turnings in the air, so as to oxidize its surface, and then reducing the surface to the metallic state, by heating the roasted turnings in a glass tube in a current of hydrogen, by which means the surface of the metal becomes very porous, and exerts a much more powerful reducing action than if it were smooth and polished.

If the organic substance contains sulphur, the process of ordinary combustion must again be slightly modified, because the sulphur, by burning in contact with the oxide of copper, is largely converted into sulphurous acid, which condenses the apparatus containing potassa, thus rendering the determination of the carbonic acid inaccurate. But the sulphurous acid is entirely retained in the combustion-tube, by placing in the anterior part of the tube a length of 0.2 m. of litharge, which, at a red-heat, absorbs sulphurous acid wholly, provided the current of gas be not too rapid.

It is also necessary to place a column of litharge in the tube, in



front of the oxide of copper, when the organic substance contains chlorine, bromine, or iodine, because, in that case, a chloride, bromide, or iodide of copper is formed, which is sufficiently volatile to permit its vapours to reach the tube containing the chloride of calcium, and falsify the determination of water. Litharge decomposes and perfectly retains these vapours at a red-heat.

The analysis of salts formed by organic acids with mineral bases the carbonates of which are indecomposable, or decompose with difficulty by heat, also requires peculiar precautions. Such bases are the alkalis and alkaline earths, which remain partly in the combustion-tube in the state of carbonates, while it cannot be admitted that they do so entirely, because the carbonates are partially decomposed by the oxide of copper, the sides of the tube, and, particularly, by the mineral acids, chlorine, and other elements which may exist in combination with the oxide of copper or with the reduced copper. The carbonic acid may be completely disengaged by substituting chromate of lead for the oxide of copper, especially if a small quantity of bichromate of potassa be added to the chromate. Otherwise, the combustion is conducted in the same manner as for the oxide of copper.

#### DETERMINATION OF NITROGEN.

§ 1217. The nitrogen contained in organic substances is determined by the process described for the analysis of the nitrates, (§ 108.) A combustion-tube *fa*, (fig. 628,) closed at one end, and about 0.8 m. in length, is used, at the bottom of which about 20 gm.



Fig. 628.

of bicarbonate of soda *ab* are placed, and above it a column *bc* of pure oxide of copper, of five or six centimetres in length, after-

ward the mixture *cd* of the organic substance with oxide of copper, and lastly a length *de* of 0.2 m. of pure oxide of copper. Over the whole is superimposed a column *ef* of 0.2 m. of metallic copper, prepared from copper turnings previously roasted in the air to oxidize their surface, and then reduced in a current of hydrogen. The tube being arranged on a long sheet-iron furnace, (fig. 629,) a glass tube, which is made to communicate with the tubulure of a small air-pump P, is fitted to its orifice by means of a cork, while to the second tubulure *d* of the pump a glass tube *def* is fastened, of which the vertical leg *ef* is about 0.8 m. in length, and the curved extremity of which dips into the small mercurial bottle B. In the first place, the air must be completely removed from the apparatus, for which purpose as perfect a vacuum as possible is made with the pump, and the stopcock *s* is closed, leaving open those at *r*, *r'*. After a few moments it is ascertained whether the

apparatus remains empty, in which case the column of mercury in the tube *ef* should remain absolutely stationary. Some coals are

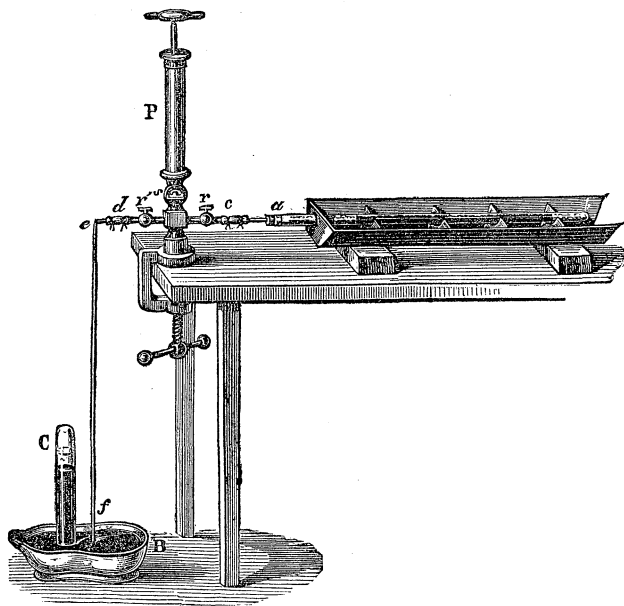


Fig. 629.

brought near the end of the tube containing the bicarbonate of soda, when the carbonic acid disengaged drives the air from the tube; and as soon as the gas begins to be evolved under the mercury, the anterior part of the tube, which contains the metallic mercury and a length of some centimetres of pure oxide of copper, is surrounded with hot coals, and it is then ascertained whether the gas which is evolved be pure carbonic acid. For this purpose it is sufficient to collect the gas in a small bell-glass filled with mercury, at the top of which a solution of potassa has been placed; and if the gas formed is pure carbonic acid, its bubbles will be immediately dissolved. When this result is obtained, the coals which effected the decomposition of the bicarbonate of soda are removed, and above the orifice of the disengaging-tube *def* a large bell-glass *C* is placed, filled with mercury, and to the top of which fifty or sixty cubic centimetres of a concentrated solution of potassa have been passed. The coals are gradually moved toward the part containing the organic matter, conducting the operation as in the determination of carbon and hydrogen. Carbonic acid, vapour of water, nitrogen and its oxides, are formed; but the oxides of nitrogen are restored to the state of free nitrogen while passing

through the portion of the tube which contains metallic copper, so that only a mixture of carbonic acid and nitrogen reaches the bell-glass, in which the carbonic acid is dissolved by the potassa, while the nitrogen remains free. When the combustion is terminated, the column of pure oxide of copper which separates the carbonate of soda from the original mixture of oxide and organic matter is surrounded with coals; and lastly, by again heating the carbonate, a new evolution of carbonic acid is produced, which completely drives the gaseous products of combustion into the bell-glass C.

It now only remains to measure exactly the nitrogen gas collected, for which purpose the bell-glass is carried over a large vessel filled with water, when, by opening the orifice of the former, the mercury contained in it falls to the bottom of the vessel, and is replaced by water. The gas is poured into a smaller bell-glass, divided into cubic centimetres, and held in a vertical direction by means of a stand, while the water on the inside and outside of the bell-glass is brought to the same level. When the gas has attained an equilibrium of temperature, its volume  $V$ , the temperature  $t$ , and the height  $H_0$  of the barometer are marked, and the weight of nitrogen gas attained is therefore

$$0.0012562 \text{ gm. } V \cdot \frac{1}{1 + 0.00367 \cdot t} \cdot \frac{H_0 - f}{760}.$$

It is important to ascertain whether the gas contains no deutoxide of nitrogen; to which effect a few bubbles of air are introduced into the bell-glass, when the gas instantly turns red if it contains any appreciable quantity of deutoxide. We shall subsequently point out the means of measuring nitrogen more exactly, and of accurately ascertaining its purity.

When the nitrous substance is volatile, the length of the column of pure oxide of copper between the mixture of the oxide with the organic matter, and the bicarbonate of soda, must be increased; and before commencing the combustion, both the anterior part of the tube and the column of pure oxide must be heated to redness.

Instead of placing at the bottom of the tube the bicarbonate of soda, intended to disengage carbonic acid, this end of the tube may be terminated by a fine tubulure, which is made to communicate, by means of caoutchouc, with an apparatus for disengaging carbonic acid, in which case the exhaustion by the air-pump may be omitted, because the evolution of carbonic acid is prolonged until all the air is driven out. When the combustion is terminated, the current of carbonic acid is re-established, in order to drive all the nitrogen into the bell-glass.

§ 1218. Nitrogen is also dosed by another process, not of so general application as the one just described, because it is not adapted to the nitrates, but which yields, in the majority of cases, exact results. This process is founded on the fact that nitrous substances, with the exception of those containing nitre or nitrous

acid, when heated in contact with hydrated alkalies, give off their nitrogen in the state of ammonia, which can be collected in an acid, and determined in the state of double chloride of platinum and ammonium. In order to effect the decomposition of the nitrous substance, a mixture of lime and hydrated caustic soda is used, which is prepared by slaking quicklime in a solution of caustic soda containing a quantity of soda equal to nearly half of that of the lime employed, after which the substance is successively ground, dried, calcined in an earthen crucible, again pulverized, and then preserved in a close bottle. We shall call it, for the sake of shortness, *soda-lime*.

An accurately weighed quantity of the organic matter is mixed with a certain quantity of soda lime, and placed at the bottom of a glass tube *abc* (fig. 630) resembling the tubes used for the combustion of organic substances by the oxide of copper, and tube is then filled with pure soda lime, while the bulb apparatus A, containing concentrated chlorohy-



Fig. 630.

droic acid, is fitted to the orifice of the tube. The tube is gradually surrounded by hot coals, as in the ordinary combustions of organic substances, the ammonia produced being dissolved in the chlorohydric acid. When the decomposition is effected, the point of the combustion-tube is broken, and, by blowing through the tube *e* of the bulb apparatus, the ammonia still remaining in the tube is driven into the chlorohydric acid. The apparatus A is then removed, the acid it contains poured into a porcelain capsule, and the apparatus washed several times with a mixture of two parts of alcohol and one of ether, which is then added to the capsule, into which an excess of bichloride of platinum is then introduced, to precipitate the ammonia as double chloride of platinum and ammonium. The precipitate is collected on a small filter, washed with a mixture of alcohol and ether, and weighed after drying: one gramme of double chloride of platinum and ammonium contains 0.06349 gm. of nitrogen.

This process of decomposition may be modified so as to obtain a more rapid, and yet very exact analysis, by placing in the bulb apparatus ten cubic centimetres of a standard solution of sulphuric acid, obtained by mixing 61.250 gm. of monohydrated sulphuric acid with one litre of water; so that 100 cubic centimetres of the liquid will saturate 2.12 gm. of ammonia, corresponding to 1.75 gm. of nitrogen. The decomposition of the nitrous substance is effected in the usual way, and the ammonia dissolves in the sulphuric acid and weakens its standard. If, therefore, the new strength of the liquid be ascertained after the operation, and the strength of the original acid subtracted from it, a difference corresponding to the quantity

of ammonia absorbed, and from which the latter may be deduced by a very simple calculation, is obtained.

The standard of the acid liquid is determined by means of a solution of saccharate of lime, that is, a solution of caustic lime in sugar and water, which dissolves a much larger proportion of lime than pure water; and the solution may be kept unchanged in well-stoppered bottles. The first step is to ascertain the number of cubic centimetres of the alkaline solution necessary to exactly saturate 10 cubic centimetres of the normal acid solution; for which purpose the 10 cubic centimetres of normal acid solution are poured into a beaker containing a small quantity of tincture of litmus; and then the solution of saccharate of lime is added by means of an alkalimeter, until the liquid turns blue, marking the number  $N$  of divisions added. In order to be very accurate, the solution of lime must be sufficiently diluted for the saturation to require about 100 divisions of the liquid. The 10 cubic centimetres of the acid solution, which have absorbed the ammonia disengaged by the decomposition of the nitrous substance, are acted on exactly in the same manner. Let us suppose that  $n$  represents the number of divisions of saccharate of lime which have effected the saturation  $\frac{n}{N}$ ; then will 0.212 gm. represent the quantity of ammonia absorbed, and  $\frac{n}{N}$  0.175 gm. the corresponding quantity of nitrogen.\*

\* Bunsen has recently introduced a new method for determining nitrogen, which, on account of its extreme exactness, especially when the substance is very nitrogenous, deserves to be described.

About 5 centigrammes of the substance, without being exactly weighed, are intimately mixed with about 5 grammes of fine oxide of copper, and a small quantity of reduced copper filings, and introduced into a very strong glass tube, difficult of fusion, of about 5 inches in length and  $\frac{3}{4}$  inches internal diameter, one end of which, having previously been drawn out, is now connected with an air-pump, after the other end has been sealed, and the air is totally exhausted from the tube; after which the other end is also hermetically sealed, and both points are strengthened in the flame by thickening the glass. The tube thus prepared is packed with plaster in a strong iron box, or coffin, the lid of which is well secured, and the whole is then exposed to a strong white-heat for several hours; when the organic substance in the tube is entirely converted into carbonic acid, water, and free nitrogen. After cooling, the tube is taken out of the iron box and brought under a graduated cylinder filled with mercury, in a mercury-trough, where one end of the tube is broken off, and the gases, consisting only of carbonic acid and nitrogen, are allowed to pass up into the cylinder. The exact volume of the two gases being now ascertained, and reduced to the corrected volume at 32° and 30 inches pressure, the carbonic acid is removed by absorbing it with a bullet of caustic potassa, fixed to the end of a platinum wire, and thus introduced into the gases through the column of mercury. After all the carbonic acid is absorbed, which is the case when a diminution of volume no longer ensues, the exact volume is again ascertained and reduced to 32° and 30 inches, when the difference will give the carbonic acid, while the gas remaining in the cylinder, and measured, is pure nitrogen.

The ratio of the nitrogen to the carbonic acid, and consequently to the carbon in the organic substance, being thus obtained, and the carbon being previously determined in the usual manner by combustion, the percentage of nitrogen may easily be calculated.—*W. L. F.*

## DETERMINATION OF SULPHUR.

§ 1219. The determination of the sulphur contained in organic substances is frequently a matter of great difficulty. Some of these substances are destroyed by contact with concentrated and boiling nitric acid, while the sulphur is converted into sulphuric acid, which is precipitated by the chloride of barium; but as many organic substances resist the action of nitric acid, the sulphur cannot always in this manner be converted into sulphuric acid.

When the organic matter is not volatile, it is mixed with 20 or 25 times its weight of a mixture of nitre and carbonate of soda, and the mixture is thrown, by small quantities at a time, into a platinum crucible heated to redness by an alcohol-lamp. The alkaline substance is then dissolved in water, supersaturated by chlorohydric acid, and the sulphuric acid precipitated by chloride of barium.

If the organic substance is volatile these processes are inapplicable, and the operation is then conducted as follows, by a method which suits all cases:—The organic matter is subjected to combustion with oxide of copper, as in the determination of carbon and hydrogen, with the exception that the combustion-tube is provided only with the bulb apparatus (fig. 631) containing a solution of caustic



Fig. 631.

potassa. The greater part of the sulphur is converted into sulphuric and sulphurous acid, which dissolve in the potassa, while a portion of the sulphur, nevertheless, remains in the combustion-tube in the state of sulphide and sulphate of copper. The tube, after being allowed to cool, is broken, and the pieces of glass and the oxide are thrown into a flask, where they are boiled with a weak solution of caustic potassa, which completely removes the sulphur and sulphuric acid. The liquid is filtered, and the potassa in the bulb apparatus is added to the filtrate, which is then boiled, and treated with a current of chlorine, which transforms all the sulphur into sulphuric acid. The solution is supersaturated by chlorohydric acid, and the sulphuric acid precipitated by chloride of barium.

## DETERMINATION OF PHOSPHORUS.

§ 1220. When the phosphuretted organic matter is not volatile, it is mixed with 20 or 25 times its weight of a mixture of carbonate of soda and nitre, and the mixture is thrown, by small portions, into a heated platinum crucible, where the phosphorus passes into the phosphate of soda. The alkaline substance is dissolved in water, saturated with chlorohydric acid, and then 1 gramme of pure iron dissolved in aqua regia is added to the solution. Lastly, the sesquioxide of iron combined with phosphoric acid is precipitated by an excess of ammonia; and by subtracting from the weight of this precipitate the weight of the sesquioxide of iron produced by 1 gm.

VOL. II.—2 H

25

of pure iron, the weight of the phosphoric acid is obtained, whence that of the phosphorus may be deduced. If the substance is volatile, it is first decomposed by carbonate of soda in a combustion-tube, and then dissolved in water, the analysis being completed as in the preceding case.

#### DETERMINATION OF CHLORINE, BROMINE, AND IODINE.

§ 1221. No organic substances have as yet been found in nature containing chlorine, bromine, or iodine, but a great number of them have been artificially produced in the laboratory. The determination of these elements is very easily made by heating the organic matter in a combustion-tube, in contact with quicklime, obtained by slaking ordinary quicklime, washing it with water to remove chlorides arising from the ashes of the combustible with which the limestone was originally burned, and then heating it to redness in order to expel the water from the hydrated lime. The lime thus prepared is preserved in a ground-stoppered bottle.

If the organic substance is solid and not volatile, it is mixed with a certain quantity of quicklime, and the mixture is introduced into the combustion-tube which is to be filled with pure lime; but if the substance is liquid and volatile, it is weighed in the glass bubbles before mentioned, which are dropped, after breaking their point, to the bottom of the tube, which is afterward filled with lime. The decomposition of the substance by heat should be effected with the same precautions as combustion by the oxide of copper. The chlorine, bromine, or iodine remain in the tube in the state of chloride, bromide, or iodide of calcium. At the close of the operation, the lime, together with the fragments of the tube, is dropped into a flask, where it is treated with weak nitric acid until the lime is entirely dissolved. The liquid is then filtered, and precipitated by nitrate of silver; the process indicated in § 1131 being followed in order to collect and wash the chloride of silver.

The determination of iodine is, however, rather more difficult, as a portion of this substance often passes into the state of iodic acid, which, however, is destroyed by passing a current of sulphurous acid through the liquid at a moderate temperature, after having added nitrate of silver to it.

#### DETERMINATION OF OXYGEN.

§ 1222. The oxygen contained in organic substances is always determined differentially, as, hitherto, a suitable process of direct determination has not been discovered. It will hence be seen how important it is to ascertain, with the greatest care, the nature of the elements composing the organic substance; for if a single element escapes the experimenter, the analysis is inaccurate, not only on account of the omission of the element which was overlooked, but

also because the weight of the elementary substance neglected is computed as oxygen.

#### ESTABLISHMENT OF THE CHEMICAL FORMULA OF AN ORGANIC SUBSTANCE.

§ 1223. The elementary analysis of an organic substance is not alone sufficient to establish its chemical formula, because it indicates only the ratios which exist between the weight of the elements which compose it; and as an infinite number of formulæ, the multiples of each other, will all satisfy the ratios given by analysis, the question is, which of these formulæ to choose. By studying the various combinations which the organic substance can form with mineral substances, and the new organic compounds to which they give rise when subjected to the various processes of the laboratory, the chemist can generally collect facts from which a formula may be deduced; and it is only when the substance has been studied under all its aspects, and in the case that it forms a great number of compounds, that its formula, and, consequently, its chemical equivalent, presents any degree of certainty. The numerous changes which, in latter years, the formulæ of organic compounds have undergone will therefore not appear surprising, being occasioned by the discovery of new compounds, or new chemical reactions, which deprive the formulæ adopted of the character of probability they had acquired from the facts previously known.

As it is impossible to advance any general rules for the establishment of the formula of an organic compound, we shall only cite a few examples, to show the spirit which governs such researches. We shall distinguish three cases: 1st, that in which the organic substance is acid; 2dly, that in which it possesses basic properties; and 3dly, that in which the organic substance is neutral.

#### CASE IN WHICH THE ORGANIC SUBSTANCE IS ACID.

§ 1224. As the first example, we shall take acetic acid, which contains only carbon, hydrogen, and oxygen.

At its maximum point of concentration, acetic acid is a colourless and volatile liquid, which, by combustion with oxide of copper, yields the following composition:\*

Hydrogen.....	6.67
Carbon.....	40.00
Oxygen.....	53.33
	<hr/> 100.00

Dividing the weight of each of these elements by its equivalent, the quotients will necessarily be to each other as the equivalent

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\* In order to render our arguments more simple, we shall always suppose that the results of the direct analyses are scrupulously exact.



numbers of the simple elements which enter into the compound, and we thus obtain :

For hydrogen.....	$\frac{6.67}{1.0} = 6.67$
“ carbon.....	$\frac{40.00}{6.0} = 6.67$
“ oxygen.....	$\frac{53.34}{8.0} = 6.67$

These quotients being equal, we shall conclude that concentrated acetic acid contains equal numbers of each of the three elements which compose it, and the most simple formula which can represent the acid is therefore  $\text{CHO}$ ; while it is evident that the formulæ  $\text{C}_2\text{H}_2\text{O}_2$ ,  $\text{C}_3\text{H}_3\text{O}_3$ ,  $\text{C}_4\text{H}_4\text{O}_4$ ,  $\text{C}_5\text{H}_5\text{O}_5$  represent equally the results of the analysis. On the other hand, we have seen that the greater part of the mineral acids, when brought to their maximum of concentration without any essential change in their chemical properties, are compounds of the anhydrous acid with one or several equivalents of water, which can be replaced by a corresponding number of equivalents of a base, and it must therefore be ascertained whether this is the case also with acetic acid. Moreover, we have seen, in the case of the mineral acids, that the knowledge of the composition of a salt formed by the acid and a mineral base of which the chemical equivalent had been previously ascertained, frequently gives the equivalent of the acid itself, and is sufficient to establish its formula. However, the example of phosphoric acid has shown that the same base frequently forms several salts with the same acid, and that it is not sufficient, to establish the formula of the acid, to determine the composition of one of these salts, because the formula would vary with the salt selected. It therefore becomes necessary to determine the composition of all the salts, either in the crystallized state, or after having dried them as much as possible, always avoiding such a change in their chemical constitution that the dried salt, when redissolved in water, will not produce the original salt by crystallization. The study of these various compounds furnishes a clue as to whether the salt should be regarded as monobasic, bibasic, tribasic, &c., and thus give the elements necessary to establish its formula. The same method must be observed in establishing the formulæ of organic acids; and we thereupon proceed to apply it to acetic acid.

Protoxide of silver is distinguished among mineral bases by the property of forming immediately anhydrous salts, which are in most cases easily obtained in a state of purity, being generally insoluble, or nearly so; for which reasons salts of silver are very valuable in ascertaining the composition of organic acids, and the more so as their analysis can be made with great accuracy. We shall therefore analyze the acetate of silver, for which purpose an accurately weighed quantity of the salt is roasted in a platinum crucible, when, the organic matter being destroyed, metallic silver re-

mains, which is weighed. The proportion of protoxide of silver to which it corresponds is then calculated, and the result will be that acetate of silver is composed of

Oxide of silver.....	69.45
Acetic acid.....	30.55
	<u>100.00</u>

Admitting that acetic acid is monobasic, that acetate of silver is anhydrous and formed of 1 equivalent of oxide of silver (116.0) and 1 equivalent of acetic acid, the equivalent of acetic acid will be deduced from the proportion :

$$69.45 : 30.55 :: 116.0 : x \text{ whence } x = 51.0.$$

Now, there is only one way of forming the number 51.0 with whole numbers of equivalents of hydrogen, carbon, and oxygen, and that is by giving to anhydrous acetic acid the formula  $C_4H_3O_3$ , and consequently, to concentrated acetic acid, the formula  $C_4H_3O_3 + HO$ , which satisfies the analysis we have given of this acid. We have, in fact,

3 eq. of hydrogen.....	3.0
4 " carbon.....	24.0
3 " oxygen.....	24.0
	<u>51.0</u>

It is, moreover, easy to ascertain that such is, in reality, the composition of the acetic acid contained in the acetate of silver. By burning this salt with oxide of copper, it will be found to contain

Oxide of silver.....	69.45
Hydrogen.....	1.80
Carbon.....	14.37
Oxygen.....	14.38
	<u>100.00</u>

Now, the formula  $AgO, C_4H_3O_3$  gives

1 eq. of oxide of silver.....	116.0	.....	69.45
3 " hydrogen.....	3.0	.....	1.80
4 " carbon.....	24.0	.....	14.37
3 " oxygen.....	24.0	.....	14.38
	<u>167.0</u>		<u>100.00</u>

But acetic acid might possibly be bibasic, and the salt of silver contain 2 equivalents of oxide of silver ; in which case the formula of the salt would be  $2AgO, C_8H_6O_6$ , that of the concentrated acetic acid  $C_8H_6O_6 + 2HO$ , and the equivalent of anhydrous acetic acid would be 102.0. The acetic acid might be tribasic, and the formula of acetate of silver  $3AgO, C_{12}H_9O_9$ , that of the concentrated acetic

2 H 2

acid  $C_{12}H_9O_9 + 3HO$ , and the equivalent of the anhydrous acetic acid might be 153.0.

Now, when an acid is bibasic, it forms two series of salts with bases: salts which contain 2 equivalents of base  $2RO$ , and salts containing 1 equivalent of base  $RO$ , and 1 equivalent of basic water. If, therefore, acetic acid were bibasic, two series of acetates would be obtained:

1st series.....  $2RO, C_8H_6O_6$ ,  
 2d series.....  $(RO + HO), C_8H_6O_9$ ;

and the salts of the second series could not lose their equivalent of basic water, without a great change in their properties.

If the acetic acid were tribasic, it should form three series of salts:—

1st series.....  $3RO, C_{12}H_9O_9$ ,  
 2d “ .....  $(2RO + HO), C_{12}H_9O_9$ ,  
 3d “ .....  $(RO + 2HO), C_{12}H_9O_6$ ;

and the salts of the two last series again could not part with their water without an important modification of their properties.

In order to decide the question, it is therefore necessary to prepare a great number of acetates, dry them as much as possible, without affecting their chemical constitution, that is, in such a manner *that the dried acetate, redissolved in water, shall reproduce the original salt by crystallization*; and lastly, subject these acetates to analysis. It will thus be found that several of these crystallized acetates contain water; but this should be considered as their water of crystallization, as it may be driven off by heat, and the dried salt, dissolved in water, reproduces, by crystallization, the original salt. The dried salts will present the composition given by the formulæ  $RO, C_4H_3O_3$ ,  $2RO, C_8H_6O_6$ ,  $3RO, C_{12}H_9O_9$ , &c.; and there being consequently no reason for regarding acetic acid as polybasic, it is considered as a monobasic acid, and the formula  $C_4H_3O_3$  has been adopted as that of the anhydrous acid.

§ 1225. For the second example in establishing the formula of an organic acid, we shall choose malic acid, which, when crystallized, is composed as follows:

Hydrogen.....	4.48
Carbon.....	35.82
Oxygen.....	59.70
	<hr/>
	100.00

Dividing the preceding numbers by their respective equivalents, there results:

For hydrogen.....	$\frac{4.48}{1.0} = 4.48$
“ carbon.....	$\frac{35.82}{6.0} = 5.97$
“ oxygen.....	$\frac{59.70}{8.0} = 7.46$

The quotients follow the ratios of the numbers 3 : 4 : 5; and the most simple formula adapted to crystallized malic acid is therefore  $C_4H_3O_5$ , while the true formula may be one of the multiples  $C_8H_6O_{10}$ ,  $C_{12}H_9O_{15}$ ,  $C_{16}H_{12}O_{20}$ , etc., etc.

The analysis of malate of silver shows that this salt contains :

Oxide of silver .....	66.67
Malic acid.....	33.33
	<hr/> 100.00

This salt does not give off water before decomposing, which leads to the supposition that it is anhydrous; and if it be regarded as formed of 1 equivalent of oxide of silver and 1 equivalent of malic acid, the equivalent of malic acid will therefore be deduced from the proportion :

$$66.67 : 33.33 :: 116.0 : x, \text{ whence } x=58$$

The combustion of the silver salt with oxide of copper gives for its composition :

Hydrogen.....	1.15
Carbon .....	13.79
Oxygen.....	18.39
Oxide of silver.....	66.67
	<hr/> 100.00

which exactly corresponds to that given by the formula  $AgO, C_4H_2O_4$ , as may be readily seen :

2 eq. of hydrogen.....	2.0	} 58.0	1.15
4 “ carbon.....	24.0		13.79
4 “ oxygen.....	32.0		18.39
1 “ oxide of silver...	116.0		66.67
	<hr/> 174.0		<hr/> 100.00

The formula of crystallized malic acid will therefore be  $C_4H_2O_4 + HO$ ; but it remains to be seen whether the acid is monobasic, in which case the formula of the crystallized acid would be  $C_4H_2O_4 + HO$ , and that of malate of silver  $AgO, C_4H_2O_4$ ;

Or, whether it is bibasic, which would give to malate of silver the formula  $2AgO, C_8H_4O_8$ , and to the crystallized acid the formula  $C_8H_4O_8 + 2HO$ ;

Or lastly, whether it is tribasic, in which case the formula of malate of silver would be  $3AgO, C_{12}H_6O_{12}$ , and that of the crystallized acid  $C_{12}H_6O_{12} + 3HO$ .

In order to decide the question, other salts formed by malic acid must be analyzed. Now, two malates of lime are known :

The formula of the first in the crystallized state is  $\text{CaO}, \text{C}_8\text{H}_{11}\text{O}_{15}$ .  
 “ second “ “  $\text{CaO}, \text{C}_4\text{H}_2\text{O}_4$ .

The first salt loses  $6\text{HO}$  by the action of heat, without change ; for, when dissolved in water, it reproduces the original salt by crystallization ; and the formula of the dried salt is therefore  $\text{CaO}, \text{C}_8\text{H}_5\text{O}_9$ , which may be written  $\text{CaO}, 2(\text{C}_4\text{H}_2\text{O}_4) + \text{HO}$ , in which case it is considered as a bimalate of lime containing 1 eq. of water of crystallization. But as this water cannot be driven off without injury to the salt, it must be regarded as basic water, and the formulæ of the malates of lime must be written,

1st malate.....  $2\text{CaO}, \text{C}_8\text{H}_4\text{O}_8$ .  
 2d malate.....  $(\text{CaO} + \text{HO}), \text{C}_8\text{H}_4\text{O}_8$ .

In this case, malic acid is considered as a bibasic acid.

An examination of the other malates leads to the same conclusion. Thus, oxide of zinc forms two malates, the composition of which, in the crystallized state, is represented by the following formulæ :

1st malate.....  $\text{ZnO}, \text{C}_4\text{H}_5\text{O}_7$ ,  
 2d malate.....  $\text{ZnO}, \text{C}_8\text{H}_8\text{O}_{12}$ ,

which, when subjected to the action of heat, lose a portion of their water without change, and become,

The 1st.....  $\text{ZnO}, \text{C}_4\text{H}_5\text{O}_4$ .  
 The 2d.....  $\text{ZnO}, \text{C}_8\text{H}_5\text{O}_9$ .

If they be further heated, they again lose water, but are altered. The formulæ of dried malates of zinc become very simple, and similar to those of malates of lime, if the malic acid be regarded as bibasic, in which case they are,

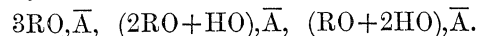
$2\text{ZnO}, \text{C}_8\text{H}_4\text{O}_8$ .  
 $(\text{ZnO} + \text{HO}), \text{C}_8\text{H}_4\text{O}_8$ .

Again, a malate of ammonia is known which crystallizes readily in beautiful crystals, and shows the formula  $(\text{NH}_3, \text{HO}), \text{C}_8\text{H}_4\text{O}_8 + \text{HO}$ . But as this salt does not lose water by heat before attaining a temperature at which it is completely altered, the water it contains is therefore basic, and its formula should be written  $(\text{NH}_3\text{HO} + \text{HO}) \text{C}_8\text{H}_4\text{O}_8$ .

All these considerations must lead us to regard malic acid as a bibasic acid, forming two series of salts, of which the formulæ are  $2\text{RO}, \text{C}_8\text{H}_4\text{O}_8$  and  $(\text{RO} + \text{HO}), \text{C}_8\text{H}_4\text{O}_8$ .

§1226. An argument of the same nature, founded on the composition of the various series of salts which the organic acid can form with the

same base, after the salts have been dried as far as their chemical constitution will permit, will decide if it be proper to regard this acid as a tribasic acid, in which case three series of salts will in general be obtained, which may be represented by the following formulæ, the symbol  $\bar{A}$  designating the equivalent of the tribasic acid:



The crystallized salts may contain, in addition, water of crystallization, which will be recognised by the fact that in most cases it can be driven off by heat, without altering the constitution of the salt.

#### DETERMINATION OF THE PROPORTION OF BASE WHICH EXISTS IN COMBINATION WITH AN ORGANIC ACID.

§ 1227. In order to establish with any degree of certainty the equivalent of an organic acid, it is necessary, as has been shown, to analyze a great number of the salts which it forms with mineral bases; and it is consequently useful to dwell for a short time on the processes employed by chemists for this purpose.

The proportion of base which exists in a salt formed by an organic acid is almost always determined by calcining the salt in the air, when the mineral base remains, either in the metallic state after the decomposition by heat, or in a state of superior oxidation, when it absorbs oxygen from the air; or lastly, in the state of carbonate, when the salt is not decomposed by the degree of heat at which the incineration took place. If the organic acid contains sulphur or phosphorus, the base may remain partly in the state of sulphate or phosphate; and if it contains chlorine, bromine, or iodine, a portion or the whole of the base may be converted into chloride, bromide, or iodide.

The salts formed by the organic acids with the alkalies, leave after calcination an alkaline carbonate; but the base is never determined in this state, because alkaline carbonates attract too readily the moisture of the air. They are converted into sulphates by pouring into the crucible in which the incineration has been effected a weak solution of sulphuric acid, taking care that the effervescence produced does not project any of the substance out of the crucible. It is evaporated to dryness; and lastly, the crucible is heated to a strong red-heat, in order to decompose the bisulphate which has formed, when the weight of the base is deduced from that of the sulphate.

When the organic salt contains baryta or strontia, the base remains in the state of carbonate, and may be weighed as such; and if it contains lime, the base still remains in the state of carbonate, if the incineration has been effected at a low temperature; but if the calcination has required a red-heat, the greater portion of the base passes into the state of quicklime. The base may still in this

case be determined as carbonate, if the precaution is taken to moisten the matter, after roasting, with a solution of carbonate of ammonia, which is then evaporated at a gentle heat. It is better to weigh the lime in the state of sulphate, to which effect the residue is moistened after incineration with sulphuric acid, and, after having driven off the excess of acid by heat, the crucible is heated to redness. The determination of magnesia in the state of sulphate should be performed in the same manner.

If the base combined with the organic acid be protoxide or sesquioxide of iron, the salt is roasted in the air; and in order to be sure that the residue is composed only of sesquioxide of iron, it is moistened with nitric acid, and again calcined; a similar process being applicable to salts of copper, in which case protoxide of copper  $\text{CuO}$  remains. Zinc, combined with an organic acid, is also determined in the state of oxide  $\text{ZnO}$ ; but the roasting must be commenced at the lowest temperature possible, in order not to produce metallic zinc, a portion of which might be lost in the state of vapour; and the roasted matter is moistened with a small quantity of nitric acid, and calcined to redness.

The determination of manganese combined with an organic acid presents some difficulties, because the composition of the oxide which remains after the calcination is never exactly known. The salt being first calcined in a small platinum boat, in order to destroy the organic matter, the boat is introduced into a porcelain tube heated to redness, and traversed by a current of hydrogen gas, which is maintained until the tube is completely cooled; when the boat, which then contains non-pyrophoric protoxide of manganese, is removed.

As the compounds of the organic acids with cobalt and nickel leave oxides after incineration, the composition of which is always uncertain, it is best to roast the salt in a platinum boat, and then heat it in a porcelain tube in a current of hydrogen, when the platinum contains the reduced metal, which is not pyrophoric if the calcination has been effected at a sufficiently high temperature.

The incineration of salts formed by the organic acids with oxides of chrome leaves pure sesquioxide of chrome, which can be immediately weighed.

By incinerating the salts formed by protoxide of lead with organic acids, the metal frequently remains in the state of protoxide, although a portion of the oxide of lead is also frequently reduced to the metallic state, so that it is better never to make these incinerations in platinum vessels, because they might be greatly injured. They are performed in porcelain capsules heated by an alcohol-lamp, so as not to attain the point of fusion of oxide of lead, which in the fused state would attack the glazing of the porcelain. After incineration, concentrated nitric acid is poured into the saucer, which disengages reddish vapours if the substance contains metallic

lead. The acid is gently evaporated, and the residue, which is composed of pure protoxide of lead, is calcined at a dull red-heat. The capsule may also be weighed after incineration, and acetic acid afterward poured into it, which dissolves the oxide of lead, and separates the metallic lead which remains in the form of small globules. The globules are washed several times, by decantation, in the capsule, which is then dried at a gentle heat; the latter is then weighed a second time, when the difference gives the weight of oxide of lead formed in the roasted matter. By weighing the capsule a third time, and subtracting this weight from that obtained by the second weighing, the quantity of lead reduced is found, which is to be converted into oxide, by calculation.

Lastly, the oxide of lead may be determined in the state of sulphate, in which case, the incinerated matter is moistened with nitric acid, which is evaporated, and then with sulphuric acid, which transforms the nitrate into a sulphate. The excess of sulphuric acid being evaporated, the sulphate is calcined to redness.

Oxide of bismuth is determined in the state of oxide  $\text{BiO}_3$ , and protoxide of tin in the state of stannic acid  $\text{SnO}_2$ , the operation being conducted as in the case of oxide of lead; that is, the substance is incinerated in a porcelain capsule, and the residue, after being moistened with nitric acid, is calcined after the evaporation of the acid.

The exact determination of oxide of antimony is very difficult. The best method consists in roasting the salt in a porcelain crucible, and, when the organic matter is burned, to cover the crucible with a lid having a hole in the centre, through which is passed the end of a disengaging-tube which conveys dry hydrogen into the crucible; when by heating the latter to redness, the oxide of antimony is reduced to the metallic state. The current of hydrogen is maintained until the crucible is completely cooled, after which the metallic antimony is weighed.

The salts formed by the protoxide and sesquioxide of uranium leave, after roasting, an oxide of uranium, the composition of which is uncertain; but if the residue be calcined, at a strong red-heat, by placing the platinum crucible which contains it in an earthen crucible heated in a charcoal fire, the oxide  $2\text{UO}, \text{U}_2\text{O}_3$  (§ 1025) remains, although it is better to restore, by means of hydrogen, the oxide of uranium to the state of protoxide, by operating as was stated for manganese.

The quantity of oxide of silver found in combination with an organic acid may be very accurately ascertained by simple incineration, which leaves the silver in the metallic state. If the salt of silver is soluble, it may be dissolved in water and the silver precipitated in the state of chloride, in which case a standard solution of common salt may also be used, and the process explained in § 1144 adopted.



Incineration also gives exactly the platinum contained in the salts formed by organic acids, when metallic platinum remains, from which the quantity of oxide may be deduced by calculation.

Salts formed by the organic acids with oxides of mercury are analyzed by the general process described § 1107.

The ammonia combined with an organic acid is generally inferred from the quantity of nitrogen yielded by the ammoniacal salt in its combustion with oxide of copper, (§§ 1217 and 1218,) although this base may be directly determined in the state of double chloride of platinum and ammonia, as in the case of ammoniacal salts formed by the mineral acids; for which purpose the ammoniacal salt is dissolved in a small quantity of water, and a slight excess of bichloride of platinum is added, when, after evaporating to dryness at a gentle temperature, and washing the residue with a mixture of alcohol and ether, the double chloride of platinum and ammonia is obtained isolated. Lastly, the ammoniacal salt may be destroyed by sodic lime at a red-heat, the ammonia collected in an acid solution, and the base determined by one of the two methods described in §§ 1217 and 1218.

§ 1228. The processes just described are applicable with absolute exactness only when the organic acid contains carbon, hydrogen, oxygen, and nitrogen alone, and their results would be frequently inaccurate if the acid contained, in addition, sulphur, phosphorus, or chlorine.

If the acid contains sulphur, the processes described may be employed whenever the sulphate of the metallic oxide is easily decomposed by heat, and the metallic sulphide is quickly changed into oxide by roasting; but in every other case some of the processes spoken of would give inexact results. When the base of the salt is an alkaline or alkalino-earthly oxide, or oxide of lead, it is sufficient to heat the incinerated substance with sulphuric acid, when the base remains in the state of sulphate, which is weighed. If the oxide forms a sulphate readily decomposable at a red-heat, the residue after roasting is calcined at this temperature, after having been treated with a small quantity of nitric acid, to prevent the presence of a metallic sulphide, which might injure the platinum crucible. In all cases it is prudent to moisten the substance, after calcination, with a small quantity of carbonate of ammonia, evaporate and recalcine it, by which means the last traces of sulphuric acid are more easily driven off.

If the organic acid contains phosphorus, all the processes described are faulty, and, in order to determine the oxide, the processes by the humid way, described under the head of each metal, must be adopted.

Lastly, if the organic acid contains chlorine, bromine, or iodine, it is often necessary to modify the ordinary processes. When the base combined with the organic acid is an alkaline or alkalino-earthly

oxide, the residue after incineration is moistened with sulphuric acid, which drives off the chlorine, bromine, or iodine, after which the excess of acid is evaporated and the substance calcined, when the base remains in the state of sulphate. This process does not always succeed easily if the base be oxide of lead, in which case it must be several times evaporated with sulphuric acid, or better still, with a small quantity of a concentrated solution of sulphate of ammonia.

The majority of the metallic chlorides, bromides, and iodides are so volatile at a red-heat that the calcination, in the air, of the organic salt containing the chlorine should be avoided; and, in order to determine the oxide, recourse must then be had to the process of determining by the humid way, described under each metal. The presence of the organic acid sometimes, however, prevents the reactions which the metallic oxide presents when combined with mineral acids, in which case the organic acid must be destroyed, either by concentrated nitric acid, when this is possible, or by mixing it with 15 or 20 times its weight of a mixture of carbonate of soda and nitre, thrown, by small quantities at a time, into a silver crucible, heated over an alcohol-lamp; when the metallic oxide is found in the alkaline residue.

#### CASE IN WHICH THE ORGANIC SUBSTANCE POSSESSES BASIC PROPERTIES.

§ 1229. All the basic organic substances, at present known, contain nitrogen. In order to ascertain their equivalent, not only the isolated bases, but also a certain number of salts which these bases form with mineral acids, must therefore be analyzed, preferring those which are most readily obtained in the crystallized form, and which can be most accurately analyzed. We shall take strychnine as an example.

The elementary analysis of strychnine yields the following results:

Hydrogen.....	6.58
Carbon.....	75.45
Nitrogen.....	8.38
Oxygen.....	9.59
	<hr/>
	100.00

Dividing the preceding numbers by the corresponding equivalent of each simple substance, there results:

For hydrogen.....	$\frac{6.58}{1.0} = 6.58$
“ carbon.....	$\frac{75.45}{6.0} = 12.57$
“ nitrogen.....	$\frac{8.38}{14.0} = 0.60$
“ oxygen.....	$\frac{9.59}{8.0} = 1.20$

The most simple ratios which exist between these quotients are as the numbers 11 : 21 : 1 : 2. The most simple formula of strychnine is  $C_{21}H_{11}N_1O_2$ .

nine is, therefore,  $C_{24}H_{11}NO_2$ ; but as the multiple of the formulæ  $C_{42}H_{22}N_2O_4$ ,  $C_{63}H_{33}N_3O_6$ , etc. etc. satisfy equally the results of the analysis, the salts of strychnine must also be analyzed.

The organic alkalies combine either with hydracids, without decomposing them, or with oxacids; in which latter case they always acquire the elements of 1 equiv. of water, which cannot be driven off without injury to the salt; and, in this respect, the organic bases behave like ammonia, in their compounds with hydracids and oxacids.

We shall first analyze the chlorohydrate of strychnine, after having dried it at  $212^\circ$ , in a current of dry air, because the crystallized salt contains water of crystallization. The elementary analysis will yield for its composition:

Hydrogen.....	6.21
Carbon.....	68.02
Nitrogen.....	7.56
Oxygen.....	8.64
Chlorine.....	9.57
	<hr/> 100.00

The determination, for itself, of the chlorine is sufficient to establish the equivalent of strychnine, admitting that the salt is constituted like the chlorohydrate of ammonia; that is, that its formula is  $Sty^+HCl$ , the symbol  $Sty^+$  representing the equivalent of strychnine. In fact, 9.57 of chlorine correspond to 9.841 of chlorohydric acid, and, consequently, 100 of chlorohydrate of strychnine contain 9.841 of chlorohydric acid, and 90.159 of strychnine; whence the equivalent of strychnine will be obtained by the proportion,

$$9.841 : 90.159 :: 36.5 : x, \text{ whence } x=334.$$

Now this equivalent corresponds to the formula  $C_{42}H_{22}N_2O_4$ , which gives

22 eq. of hydrogen.....	22.0
42 " carbon.....	252.0
2 " nitrogen.....	28.0
4 " oxygen.....	32.0
	<hr/> 334.0

The formula of free strychnine is therefore  $C_{42}H_{22}N_2O_4$ , and that of the dried chlorohydrate  $C_{42}H_{22}N_2O_4.HCl$ . The crystallized base is anhydrous. It is easy to ascertain, by calculating the composition of the chlorohydrate of strychnine in hundredths, from the formula just given, that there result, for each element, numbers identical with those above transcribed, and which we have supposed to be obtained by direct analysis.

The formula of strychnine may be verified by the analysis of

other salts of the base, as, for example, that of the sulphate. The formula of crystallized sulphate of strychnine, dried at  $266^{\circ}$ , is thus found to be  $(C_{42}H_{32}N_2O_4, HO), SO_3$ .

§ 1230. The quantity of mineral acid which exists in combination with an organic alkali is determined by the same means as those used to determine the acid in a mineral salt; but the analysis demands the greatest care, because the smallest error may seriously affect the generally very complicated formula of the organic alkali. In order to determine the quantity of chlorohydric acid which exists in chlorohydrate of strychnine, the chlorohydric acid is first determined by precipitating it in the state of chloride of silver, in the manner stated in § 1131. The weight obtained is generally too small. Admitting, for the moment, the weight obtained to be exact, from this weight may be calculated the quantity of pure silver which would exactly precipitate the chlorohydric acid contained in 5 grammes of chlorohydrate of strychnine. The silver is dissolved in nitric acid, and the liquid poured into a solution of 5 grammes of chlorohydrate of strychnine; after which the solution, when clear, is filtered, and, by the assistance of a decimal solution of silver, the quantity of chlorohydric acid which still remains in the liquid is determined, (§ 1144.) Salts formed by the other mineral acids can be analyzed by analogous processes.

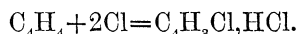
The compounds which the chlorohydrates of organic bases form with bichloride of platinum are frequently subjected to analysis, by being precipitated in the form of small yellow granular crystals. The composition of the double chloride of platinum and strychnine is analogous to that of the double chloride of platinum and ammonia, and its formula is  $(C_{42}H_{32}N_2O_4)HCl + PtCl_2$ . By roasting this and similar compounds in the air, the organic matter is destroyed and the chlorine disengaged, while the platinum remains; which process is well adapted to the determination of the equivalent of the organic base, and is capable of great exactness, on account of the great weight of the equivalent of platinum.

#### CASE IN WHICH THE ORGANIC SUBSTANCE IS NEITHER ACID NOR BASIC.

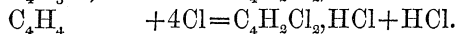
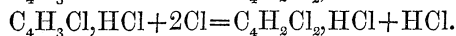
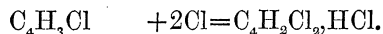
§ 1231. When the simple organic substance possesses neither acid nor basic properties, there is no general rule for establishing its equivalent and its formula; and chemists are then guided by the composition of the products of combination, or decomposition, to which the substance gives rise under the influence of various chemical agents. They choose, among all the equivalent formulæ, that which expresses most simply the whole of the reactions, frequently giving preference to the formula which establishes an analogy of constitution with other substances presenting similar reactions. We shall be satisfied with two examples, which we shall select from the most simple.

The method of preparing bicarburetted hydrogen or olefiant gas has already been shown, (§ 266.) The most simple formula which satisfies the direct analysis of this gas is  $\text{CH}$ , and we will proceed to show why the formula  $\text{C}_4\text{H}_4$  has been assigned to it.

By mixing in a large bell-glass equal volumes of olefiant gas and chlorine, a liquid substance condenses, of which the most simple formula is  $\text{C}_2\text{H}_2\text{Cl}$ , and which, by treatment with an alcoholic solution of caustic potassa, loses one-half of its chlorine, and one-fourth of its hydrogen, in the state of chlorohydric acid, which combines with the potassa ( $\text{KO} + \text{HCl} = \text{KCl} + \text{HO}$ ); while at the same time a very volatile substance is formed, of which the most simple formula is  $\text{C}_4\text{H}_3\text{Cl}$ . It is but natural to regard the chlorine and hydrogen, which were separated in the state of chlorohydric acid, as united in the compound  $\text{C}_2\text{H}_2\text{Cl}$ , differently from the other portions of chlorine and hydrogen which remain, and which enter into the constitution of the compound  $\text{C}_4\text{H}_3\text{Cl}$ ; but chemists have gone still further in admitting that the chlorine and hydrogen removed by the action of the potassa existed really in the state of chlorohydric acid in the substance  $\text{C}_2\text{H}_2\text{Cl}$ ; and, in order to avoid fractional numbers of equivalents, they replace the formula  $\text{C}_2\text{H}_2\text{Cl}$  by the multiple formula  $\text{C}_4\text{H}_4\text{Cl}_2$ , which they write  $\text{C}_4\text{H}_3\text{Cl}, \text{HCl}$ . If the formula  $\text{C}_4\text{H}_4$  is assigned to olefiant gas, the reaction of chlorine on this substance is expressed in the most simple manner possible, by the following equation:



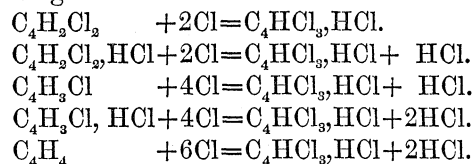
Now, if chlorine is made to act on the substance  $\text{C}_4\text{H}_3\text{Cl}$ , or on the compound  $\text{C}_4\text{H}_3\text{Cl}, \text{HCl}$ , a new substance is formed, of which the most simple formula is  $\text{C}_4\text{H}_3\text{Cl}_3$ , which, when treated by an alcoholic solution of potassa, gives off 1 equiv. of hydrogen and 1 equiv. of chlorine. We shall regard these equivalents as existing in the state of chlorohydric acid in the substance  $\text{C}_4\text{H}_3\text{Cl}_3$ , as we have done for the substance  $\text{C}_4\text{H}_4\text{Cl}_2$ , and shall write the formula of the new compound  $\text{C}_4\text{H}_2\text{Cl}_2, \text{HCl}$ . The reactions by which it is derived either from the substance  $\text{C}_4\text{H}_3\text{Cl}$ , or from the compound  $\text{C}_4\text{H}_3\text{Cl}, \text{HCl}$ , or lastly, from the olefiant gas  $\text{C}_4\text{H}_4$ , are of the most simple character.



In the last two cases, 1 equiv. of chlorohydric acid is set free.

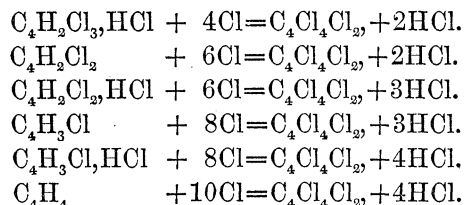
The product  $\text{C}_4\text{H}_2\text{Cl}_2$ , or the compound  $\text{C}_4\text{H}_2\text{Cl}_2, \text{HCl}$ , being submitted, in their turn, to the action of chlorine, yields a new product, of which the most simple formula is  $\text{C}_2\text{HCl}_3$ . If we write this formula  $\text{C}_4\text{H}_2\text{Cl}_4$ , and if we give it the form  $\text{C}_4\text{HCl}_3, \text{HCl}$ , the reactions which produce it by the action of chlorine on the various

substances  $C_4H_2Cl_2$ ,  $C_4H_2Cl_2, HCl$ ,  $C_4H_3Cl$ ,  $C_4H_3Cl, HCl$ , and  $C_4H_4$ , are the following:



The compound  $C_4HCl_3, HCl$  is also decomposed by contact with the alcoholic solution of potassa, but the substance  $C_4HCl_3$  has not yet been obtained in a state of purity, and seems to be altered itself by the alcoholic solution of potassa. It cannot the less be admitted that this substance pre-exists in the compound  $C_4H_2Cl_2$ , for the very reason that this establishes perfect uniformity in all the derived compounds—a uniformity which, moreover, has hitherto been destroyed by no other reaction.

Lastly, the substance  $C_4HCl_3, HCl$ , when subjected to the action of chlorine, assisted by solar light, parts with the whole of its hydrogen, which is disengaged in the state of chlorohydric acid, while a crystalline compound, which is a simple chloride of carbon, the most simple formula of which is  $C_2Cl_3$ , is formed. Various chemical reactions show that one of the equivalents of chlorine is not as deeply interested in the compound as the other two. Removing, for example, this equivalent by an alcoholic solution of monosulphide of potassium, a new chloride of carbon, of which the most simple formula is  $CCl$ , will separate, to which, for the moment, we will give the formula  $C_2Cl_2$ , in which case the first could be written  $C_2Cl_2, Cl$ . But it would be more proper to write their formulæ  $C_4Cl_4$  and  $C_4Cl_4, Cl_2$ , because, with these last formulæ, the reactions which give rise to the chloride of carbon  $C_4Cl_4, Cl_2$ , by the action of chlorine on all the successive compounds of which we have previously established the formulæ, are of the most simple kind:



We will remark, in addition, that olefiant gas  $C_4H_4$ , and all the chlorinated products  $C_4H_3Cl$ ,  $C_4H_2Cl_2$ ,  $C_4HCl_3$ ,  $C_4Cl_3$ , derived from it, present this remarkable property, that they may be regarded as *one and a single molecular grouping*  $C_4H_4$ , modified only by the successive substitution of an equal number of equivalents of chlorine for its equivalents of hydrogen. This fact is again corrobo-

rated by the following: *If the substances are operated on at a temperature sufficiently high to allow all of them to exist in the gaseous state, the formulæ  $C_4H_4$ ,  $C_4H_3Cl$ ,  $C_4H_2Cl_2$ ,  $C_4HCl_3$ ,  $C_4Cl_4$  would represent the same volume of these various gases; each of these formulæ corresponding, in fact, to 4 volumes of the vapour of the body to which it relates.*

The comparisons and similarity of composition just pointed out among all these substances would disappear, if for each of them equivalent formulæ more simple than those we have admitted were adopted, although they would still exist if equivalent formulæ were admitted, multiples of those just established; but there is no reason whatever for thus complicating the formulæ.

§ 1232. For the second example we shall choose alcohol, which liquid is composed as follows:

Hydrogen.....	13.05
Carbon.....	52.17
Oxygen.....	34.78
	<hr/> 100.00

Dividing each of these numbers by the equivalent of the substance to which it belongs, the following quotients result:

For hydrogen.....	$\frac{13.05}{1.0} = 13.05$
“ carbon.....	$\frac{52.17}{6.0} = 8.69$
“ oxygen.....	$\frac{34.78}{8.0} = 4.35$

The ratio of these quotients to each other being that of the numbers 3 : 2 : 1, the most simple formula which can be given to alcohol is  $C_2H_3O$ , while all its multiple formulæ represent equally well the results of the analysis.

Alcohol is a substance possessing neither acid nor basic properties; and as its equivalent and chemical formula cannot therefore be established by the methods described for the acids and bases, resort must be had to the chemical reactions which ensue when alcohol is subjected to the various agents in the laboratory, and from these the formula which explains them all in the simplest manner must be deduced.

By mixing together equal parts of alcohol and sulphuric acid, and exposing the mixture for several hours to a temperature of  $120^\circ$  or  $140^\circ$ , a compound acid is obtained containing sulphuric acid and some of the elements of alcohol. This acid, called *sulphovinic*, forms readily crystallizable salts with bases, and, as it is an acid, its equivalents and consequently its formula, can be determined by the methods explained, (§ 1224.) The result is then found that the formula of anhydrous sulphovinic acid, that is, of the acid as it exists in salts which contain no water of crystallization, is  $C_4H_5O$ ,  $2SO_3$ ; and if the formula  $C_2H_3O$  is assigned to alcohol, the reaction

which produces sulphovinic acid is not explained in a simple manner, as it is then supposed that the reaction takes place between 2 equivalents of sulphuric acid, and 2 equivalents of alcohol  $C_2H_5O$ , one of which does not behave in the same manner as the other. If, on the contrary, the equivalent formula  $C_4H_6O_2$  be adopted for alcohol, the reaction is of the most simple kind: 1 equivalent of alcohol gives off 1 equivalent of hydrogen and 1 equivalent of oxygen in the state of water, while the product  $C_4H_5O$ , remaining after this separation, combines with 2 equivalents of sulphuric acid to form sulphovinic acid  $C_4H_5O, 2SO_3$ , which retains in combination the equivalent of water separated, to form hydrated sulphovinic acid  $C_4H_5O, 2SO_3 + HO$ .

By distilling the mixture of alcohol and sulphuric acid in a retort, a very volatile liquid, called *ether*, passes over, the most simple formula of which is  $C_4H_5O$ . Now, it will be seen that if the formula  $C_4H_6O_2$  for alcohol be adopted, ether is derived from it simply by the abstraction of 1 equivalent of water; and the facility with which alcohol loses 1 equivalent of hydrogen and 1 of oxygen, which separate in the state of water, has led many chemists to admit the existence in this body of 1 equivalent of water ready formed, and to, consequently, regard alcohol as a combination of 1 equivalent of ether and 1 of water, and to write its formula  $C_4H_5O, HO$ .\* But is it more suitable to adopt for ether its most simple formula  $C_4H_5O$  or an equivalent multiple formula? This question must be answered by the chemical reactions of the substance. Now, ether combines with the mineral acids, and the resulting compounds, called *compound ethers*, should not be considered as salts, because they have none of their characteristic properties, but rather as definite compounds, of which the composition should be simply expressed by the assistance of the formula adopted for ether. Now, there is known

A nitric ether.....	$C_4H_5O, NO_5$ ,
A carbonic “ .....	$C_4H_5O, CO_2$ ,
An oxalic “ .....	$C_4H_5O, C_2O_3$ ,
An acetic “ .....	$C_4H_5O, C_4H_3O_3$ :

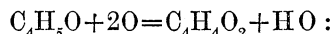
the formula  $C_4H_5O$  adopted for ether, gives to all these compounds the most simple formulæ possible.

Ether, subjected to an oxidizing agency, gives off its water and is converted into a new substance, called *aldehyde*, of which the most simple formula is  $C_2H_2O$ , but which is written  $C_4H_4O_2$ , be-

\* Since the original was written, Mr. Frankland has succeeded in isolating, by decomposing iodic ether, or iodide of ethyl,  $C_2H_5I$ , with zinc, the until then hypothetical substance ethyl, which thus must be considered as a compound organic radical, corresponding to a metal in mineral chemistry, and of which ether is the oxide, while alcohol then necessarily must be regarded as its hydrate.—*W. L. F.*

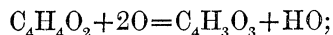


cause the reaction which produces it is then expressed in the most simple manner by the equation



the molecular constitution of aldehyde is therefore the same as that of ether, there being simply a substitution of 1 equivalent of oxygen for 1 equivalent of hydrogen.

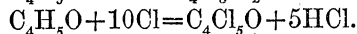
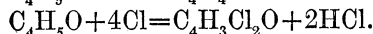
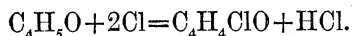
The oxidizing agency being still continued, aldehyde is converted into acetic acid, the formula of which, from its acid properties, may be determined according to § 1224. It has been shown that anhydrous acetic acid, as it exists in salts, is  $\text{C}_4\text{H}_3\text{O}_3$ . Now, the new reaction is again expressed in the most simple manner, by admitting the formula  $\text{C}_4\text{H}_5\text{O}$  for ether, and the formula  $\text{C}_4\text{H}_4\text{O}_2$  for aldehyde; and acetic acid is in fact derived from aldehyde by a reaction similar to that which transforms ether into aldehyde:



the equivalent of water formed remaining combined with the acetic acid, and giving to the latter its maximum of concentration. In acetic acid, as in aldehyde, the molecular constitution of ether is preserved, a new equivalent of hydrogen being merely replaced by 1 equivalent of oxygen.

Alcohol, subjected to oxidizing agencies, furnishes the same products as ether; that is, aldehyde at first, and subsequently acetic acid, which is one of the reasons which have confirmed chemists in regarding alcohol as a hydrate of ether.

Lastly, ether, when subjected to the action of dry chlorine, and exposed to solar light, yields a series of products, of which the most simple formulæ are  $\text{C}_4\text{H}_4\text{ClO}$ ,  $\text{C}_4\text{H}_3\text{Cl}_2\text{O}$ ,  $\text{C}_4\text{Cl}_5\text{O}$ , which substances are derived from ether  $\text{C}_4\text{H}_5\text{O}$ , by reactions resembling those which take place in the action of oxygen, and which are expressed by the equations:



The new substances  $\text{C}_4\text{H}_4\text{ClO}$ ,  $\text{C}_4\text{H}_3\text{Cl}_2\text{O}$ ,  $\text{C}_4\text{Cl}_5\text{O}$  present the same molecular constitution as ether  $\text{C}_4\text{H}_5\text{O}$ ; 1, 2, or 5 equivalents of hydrogen of the original ether being replaced by 1, 2, or 5 of chlorine.

Numerous additional examples of products derived from ether under the influence of various chemical agents might be given, and in all cases it would be found that the reactions explain themselves in the most simple and natural manner, by adopting the formula  $\text{C}_4\text{H}_5\text{O}$  for ether, and, as none of the explanations would become more simple if an equivalent multiple formula were substi-

tuted for the one adopted, the formula  $C_4H_5O$  for ether must be considered as established, and consequently the formula  $C_4H_6O_2$  or  $C_4H_5O,HO$  for alcohol. These formulæ being once admitted, those of all the products of ether and alcohol, which have just been mentioned, are equally established.

§ 1233. In the preceding remarks, the results of the chemical analyses have been supposed to be absolutely accurate, which, however, is rarely the case, as the most carefully conducted analysis is liable to trifling errors, which frequently leave the chemist uncertain as to the formula he should adopt for the substance analyzed, when the latter contains a great number of equivalents of its elementary principles, and when, consequently, its equivalent is very high. This uncertainty can be removed only by a new analysis, more carefully conducted, operating on larger quantities of matter, and directing the operations chiefly with the intention of ascertaining exactly the element of which the number of equivalents is most uncertain. It is also frequently sought to determine with most exactness the atomic weight of the compound, by using the *method of successive approximation*, of which an example has been given (§ 1230) in the determination of the chlorine contained in the chlorhydrate of strychnine.

The chemist is also guided by the probable analogies of constitution which should exist between the substances of which he seeks the formula, and other substances presenting notorious resemblances in their chemical properties with the first, and the formulæ of which are already established.

We shall observe, subsequently, *that all organic compounds, of which the composition and formula are known with some degree of certainty* (and the number of them is quite large) *contain, in their equivalent, an even number of equivalents of carbon.* This fact is certainly not accidental, and renders it very probable *that for the equivalent of carbon, a number double of that which has been hitherto admitted must be adopted.* The number 6.0 has been adopted as the equivalent of carbon, on account of the compounds which this substance forms with oxygen, as these compounds are thus represented :

Oxide of carbon by the formula.....	CO.
Carbonic acid                   “ .....	CO <sub>2</sub> .
Oxalic acid                   “ .....	C <sub>2</sub> O <sub>3</sub> .

Oxalic acid alone, of these compounds, contains an even number of equivalents of carbon, and consequently belongs to the category of other organic substances. No means is known of fixing directly the value of the equivalent of oxide of carbon, because this substance is neutral and forms no well-marked compound; and the formula  $C_2O_3$  might therefore, without any inconvenience, be adopted for

oxide of carbon. The equivalent of carbonic acid is deduced from the analysis of the carbonates. Now, two series of carbonates are known, which, with the equivalent of carbon now adopted, are written  $\text{RO}, \text{CO}_2$ ,  $\text{RO}, 2\text{CO}_2$ . But it has not yet been decided with certainty which of this series should be considered as containing the neutral carbonates. If, contrary to what the majority of chemists have admitted, we were to regard the second series as that of the neutral carbonates, we must write the formula of the two series  $2\text{RO}, \text{C}_2\text{O}_4$ ,  $\text{RO}, \text{C}_2\text{O}_4$ ; and carbonic acid would then contain also an even number of equivalents of carbon.

Be this as it may, the chemist will necessarily regard the general observation we have just made, and avoid adopting a formula which contains an uneven number of equivalents of carbon.

#### DETERMINATION OF THE DENSITY OF THE VAPOURS OF VOLATILE SUBSTANCES.

§ 1234. It has already been shown, in the preceding parts of this work, that in the combinations of elementary gases there always exists a very sensible ratio between the volumes of these gases; and that when the resulting compound itself is gaseous, a very simple ratio between its volume and the sum of the volumes of the component gases is observed. This law applies not only to substances which are gaseous at the ordinary temperature, but probably to all volatile substances, if they are observed at a temperature sufficiently high for them to exist in the state of vapour, and if this temperature is sufficiently above the point of liquefaction to enable the vapour to follow, at least by approximation, the laws of expansion and elasticity admitted for the permanent gases. It has been shown, moreover, that in the compound gases to which similar chemical formulæ are assigned, the equivalents are represented by the same number of volumes of vapour. Thus chlorohydric, bromohydric, and iodohydric gas, resulting from the combination of 2 volumes of hydrogen with 2 volumes of gaseous chlorine, bromine, and iodine, have, as their equivalents in volume, 4 volumes of gas. The equivalents which we shall be led to adopt for the numerous carburetted hydrogens, if we are guided by considerations analogous to those advanced in § 1231 for olefiant gas, are all represented by 4 volumes of vapour. The equivalent of gaseous alcohol is represented by 4 volumes, if we adopt for its formula  $\text{C}_4\text{H}_6\text{O}_2$ . The chemical reactions of several organic substances are perfectly analogous to those of alcohol; and the formulæ which we are led to adopt for them, from considerations analogous to those indicated, (§ 1232,) fix their gaseous equivalents at 4 volumes.

Ether, to which we assign the formula  $\text{C}_4\text{H}_{10}\text{O}$ , is represented by 2 volumes of vapour, and consequently the organic substances, the chemical reactions of which are analogous to ether, are also represented by two volumes of vapour.

It will from this be understood that the density of the vapours of volatile compounds furnishes, in a great number of cases, data valuable in guiding the choice of their chemical formulæ, especially when such compounds have been but little studied, and but a small number of their chemical reactions (and these not very well marked) are known.

Some volatile substances yield vapours which obey the laws of permanent gases, starting at temperatures raised only  $70^{\circ}$  or  $100^{\circ}$  above their boiling point; while other vapours, on the contrary, only obey these laws approximately, when they are heated  $360^{\circ}$  or  $450^{\circ}$  above this point. Now, as the laws which govern the combinations of gaseous bodies exist rigorously, only under circumstances in which the gases follow the law of Mariotte in their elasticities, and present equal coefficients of expansion, it will be necessary, in determining the density of a vapour, compared with that of atmospheric air under the same circumstances of temperature and pressure, to ascertain if the density found at one temperature remains the same at temperatures which differ less than  $90^{\circ}$  or  $108^{\circ}$ ; and it is only when this condition is satisfied that the vapour can be admitted to belong to the permanent gases, and that the formula of the substance may be established on the density of its vapour.

We will adduce a few examples in support of the truth of what has just been said.

Monohydrated acetic acid  $C_4H_3O_3 + HO$  boils at  $240^{\circ}$  under the ordinary pressure of the atmosphere; and the density of its vapour, compared with atmospheric air under the same circumstances of pressure and temperature, have been found at

257° .....	3.180	392° .....	2.248
266 .....	3.105	428 .....	2.132
284 .....	2.907	464 .....	2.090
302 .....	2.727	518 .....	2.088
320 .....	2.604	590 .....	2.085
338 .....	2.480	608 .....	2.083
356 .....	2.438	637 .....	2.083
374 .....	2.378		

It will be seen that the density of this vapour diminishes continually to the temperature of  $464^{\circ}$ , which is  $216^{\circ}$  above the boiling point of the substance. But it will also be seen that from  $464^{\circ}$  to  $637^{\circ}$  the density does not sensibly vary: this constant value of the density must therefore be adopted when the vapour of acetic acid is compared with the permanent gases.

In a great number of other volatile substances, the density of the vapour attains its constant value at a few degrees above its boiling point: thus for alcohol, which boils at  $173.3^{\circ}$ , the following densities of vapour have been found:

190.4°.....	1.725	302°.....	1.604
208.4 .....	1.649	347 .....	1.607
230 .....	1.610	392 .....	1.602
257 .....	1.603		

From 230°, which is only about 56° above the boiling point, the vapour of alcohol preserves an almost constant density.

§ 1235. The density of a vapour is the ratio between the weight of a certain volume of this vapour and that of the same volume of atmospheric air, under the same circumstances of temperature and pressure. The weight of a given volume  $V$  of atmospheric air, at a known temperature and under a known pressure, is easily determined. If the temperature is expressed by  $T$ , and the pressure by  $H_0$ , the weight  $P$  of the volume  $V$  of air will be, supposing  $V$  to represent the volume expressed in cubic centimetres,

$$P = 0.0012932 \text{ gm. } V \cdot \frac{1}{1+0.00366T} \cdot \frac{H_0}{760}.$$

The elastic force  $H_0$  is supposed to be represented by the height of the column of mercury at 32°, which will balance it, expressed in millimetres, while  $T$  represents the centigrade temperature of an air thermometer.

To obtain the density of a vapour, it is, therefore, sufficient to determine the weight  $P'$  of a known volume  $V$  of this vapour, at a temperature  $T$  and under a pressure  $H_0$ . Two different methods are used for this purpose: in the first, the volume occupied by a known weight  $P'$  of the volatile substance, at the temperature  $T$  and under the pressure  $H_0$ , is measured: while in the second method, on the contrary, the substance is vaporized in a flask, of which the volume is known *à priori*, and the weight of the vapour which fills it is determined by experiment.

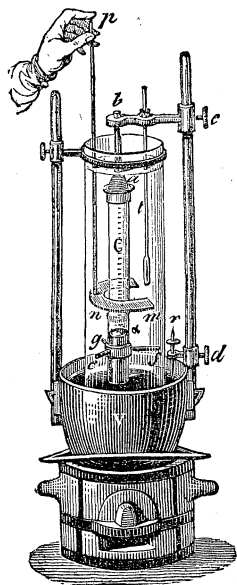


Fig. 632.



Fig. 633. is filled with water, if the temperature

is not to exceed  $212^{\circ}$ , while a thermometer  $t$  is so kept in the water that the mercurial column is always under the level of the liquid. The diameter of the cylinder should be 5 or 6 centimetres less than that of the pot, so that the atmospheric pressure may be directly exerted on a circular surface of mercury, comprised between the outside of the cylinder and the inside of the pot, and of which the level may be accurately ascertained by a double-pointed screw  $r$ , the lower point of which is in exact contact with the surface in the mercury.

The kettle being placed on the furnace, the temperature is gradually raised, when the expansion of the liquid soon breaks the glass globe; and, when the temperature is sufficiently elevated, the liquid is converted into vapour, which depresses the mercury in the bell-glass. The heat is continued until the water in the cylinder boils, after which the volume occupied by the vapour and the pressure to which it is subjected are accurately noted down. In order to obtain the latter datum, the lower point of the screw is brought to the exact level of the surface of the mercury between the cylinder and the kettle, and, by means of a cathetometer, the difference of level between the surface of the mercury in the bell-glass and the upper point of the screw is determined, to which length must be added that of the screw already known *à priori*, in order to obtain the height  $h$  of mercury which, in addition to the elastic vapour, balances the external barometric pressure. The column  $h$  of mercury, reduced by calculation to  $32^{\circ}$ , being subtracted from the height of the barometer, also reduced to  $32^{\circ}$ , will give the elastic force  $H'$ , of the vapour.

The fact that the cylinder surrounding the bell-glass is rarely perfectly cylindrical, gives rise to deviations in the luminous rays, which may affect the determination of the height  $h$ , by means of the cathetometer, while the cylinder is filled with water. To be sure of this, the micrometric wire of the telescope of the cathetometer is directed over the division of the bell-glass nearest to the level of the mercury inside, and the water is then removed from the cylinder by means of a siphon; when it is easy to ascertain whether the wire of the micrometer remains over the division, in which case the interposition of the liquid filling the cylinder has certainly produced no abnormal deviation of the ray. If there has been any displacement, the micrometer is again brought over the same division, and the distance travelled by the vernier of the instrument then gives the correction to be made in the height  $h$  observed in the first case.

When no cathetometer is at hand, the simplest way of determining the height  $h$  consists in carefully marking the position of the inner level of the mercury on the divisions of the bell-glass, and levelling exactly the external circular surface of the bath with the lower point of the screw  $r$ . The water is then entirely removed from the cylin-

der, the last drops being soaked up by tissue-paper, and then mercury is poured into the kettle, so as again to bring the external surface of the mercury on a level with the point. As the mercurial bath is on the same level, both on the inside and outside of the cylinder, it suffices to mark on the bell-glass the division to which the level reaches. The height  $h$  is then equal to the distance between this division and that at which the level of the mercury on the inside of the bell-glass stops at the moment of measuring the volume of a vapour.

If the substance boils at a very low temperature, the density of its vapour is sometimes determined at a temperature below  $212^{\circ}$ ; and it is then sought to render stationary the temperature of the water in the cylinder at the exact temperature at which the volume of vapour is to be observed. By properly regulating the fire under the kettle, a moment arrives at which the apparatus receives from the furnace a quantity of heat equal to that which it loses from its whole surface by contact with the surrounding air, and by the vaporization of the water in the cylinder; which period, frequently lasting 8 or 10 minutes, is chosen for the observation. The water must be constantly stirred with the agitator *p<sub>mn</sub>*, in order to obtain a uniform temperature throughout.

If it is required to observe the volume of a vapour at a temperature above  $212^{\circ}$ , the water in the cylinder is replaced by a fixed oil, which should be as colourless and transparent as possible; but the experiment is then more difficult and the results less exact. The oil, of which the capacity for heat is much less than that of water, cools rapidly in the air, and, in order to obtain a high stationary temperature in the oil-bath, the mercury in the kettle must be heated to a greater degree, and, therefore, evolves copious vapours, which must be avoided. It is also a matter of uncertainty whether the temperature of the column of mercury, which is raised in the bell-glass, and stands in immediate contact with the vapour the volume of which is to be found, is not higher than that of the surrounding oil; and, lastly, if the tension of the mercurial vapour can be neglected, without any appreciable error, for temperatures below  $212^{\circ}$ , (for at this temperature it only reaches a  $\frac{1}{2}$  millimetre,) this is not the case when high temperatures are necessary; and the tension of the mercury must then also be taken into account, by being added to the elastic force of the vapour. For these various reasons, the process just described is not so well adapted to temperatures above  $300^{\circ}$  or  $350^{\circ}$ .

§ 1236. The second method is applicable, on the contrary, to any temperature whatever; and the only difficulty it presents is that of procuring vessels to hold the vapour, which are not misshapen, or liable to injury when exposed to a very high temperature.

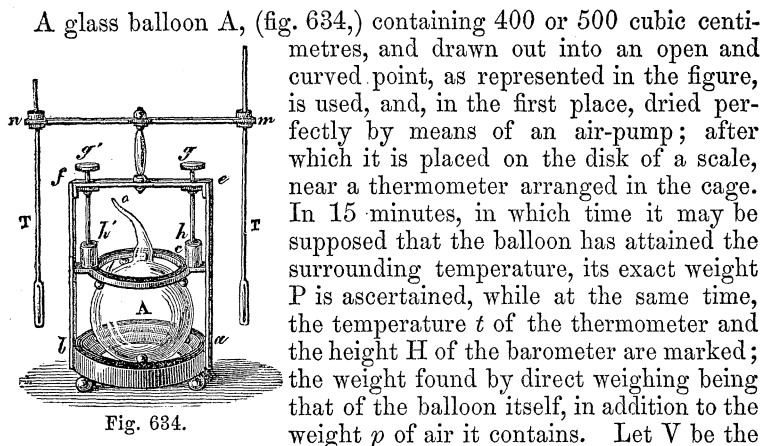


Fig. 634.

capacity of the balloon expressed in cubic centimetres, then will the weight  $p$  of the air which it contains be

$$p = 0.0012932 \cdot V \cdot \frac{1}{1 + 0.00367 \cdot t} \cdot \frac{H_0}{760};$$

and the weight of the balloon alone is therefore  $(P - p)$ .

About 10 grammes of the liquid, the density of whose vapour is to be determined, being introduced into the balloon, the latter is fastened on a copper support, with its tubulure upward, to facilitate the escape of the air which is expelled by the vapour developed during the experiment. This support may be variously shaped: in fig. 634 it is composed of two metallic rings, the lower one of which  $ab$  is supported by three small feet which keep it at a distance of 3 centimetres from the floor, while it is provided with two grooved uprights  $ae$ ,  $bf$ , fastened together by a crosspiece  $ef$ . The upper ring  $cd$  has two ears, which slide in the grooves of the uprights  $ae$ ,  $bf$ ; and the balloon  $A$  is fitted between the two rings, and held firmly by two corks  $h$ ,  $h'$ , which are pressed by two screws  $g$ ,  $g'$ . A vertical piece has a movable crosspiece  $mn$ , serving to support two thermometers  $T$ ,  $T$ , of which the bulbs should be at the height of the centre of the balloon. As the crosspiece  $mn$  is movable, various positions in the bath can be given to the thermometers, in order to ascertain whether the temperature of the latter be the same throughout.

The liquid bath in which the balloon is heated is contained in a cast-iron kettle placed over a furnace. When the temperature is not to exceed  $212^\circ$ , the kettle is filled with water, while, if it is comprised between  $212^\circ$  and  $257^\circ$ , it should contain a solution of chloride of calcium. When a temperature of from  $257^\circ$  to  $302^\circ$  is required, a fixed oil is used, giving the preference to animal oils, such as neatsfoot oil, as they yield less vapour at the same temperature, and their vapours are less acid than those of vegetable oils.



Lastly, if the operation demands a still higher temperature, metallic baths, formed of alloys of lead, bismuth, and tin, are employed.

Fig. 635 represents a more simple apparatus than that of fig. 634, and which possesses some advantages over the latter. It is composed of an iron rod  $tp$ , fastened by means of a thumbscrew to

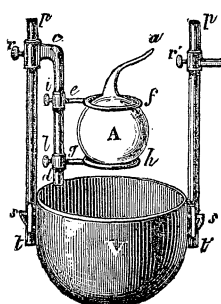


Fig. 635.

one of the ears  $s$  of the kettle  $V$ . Along the rod  $tp$  slides a piece of bent iron  $cd$  terminating below by a ring  $gh$ , on which the balloon  $A$  rests; while a second ring  $ef$ , fastened to an iron rod, slides along the rod  $cd$ , and may be fastened to it at any height by a thumbscrew  $i$ , serving to hold the balloon in a fixed position. It is sufficient to slide the movable part  $cd$  of the support along the upright  $tp$  to cause the balloon to dip into the kettle  $V$ , where it is then secured by the thumbscrew  $r$ . When the metallic bath is used, it should be

brought to the liquid state before dipping the balloon into it.

A second iron rod  $t'p'$ , fastened to the ear  $s'$ , holds the air thermometer  $B$ , resembling that which will be described in a note at page 414.

The bath is gradually heated, taking care that the temperature shall constantly rise; and when the liquid contained in the balloon has boiled, it begins to distil, and its vapour drives off the air contained in the vessel, which partly escapes by the point  $a$ . If the substance be valuable, the greater portion of that which is evolved can be collected, by introducing the point  $a$  into a small tube closed at one end. The temperature is then raised until the point at which the examination is to be made is approached, when all the doors of the furnace are closed, and, stirring the bath constantly, the moment is awaited when the temperature becomes stationary. The temperature being marked, the flame of an alcohol lamp is passed under that part of the stem of the balloon which projects from the fluid, in order that no condensed drops shall remain; after which the point  $a$  is quickly closed, and the height  $T'$  of the barometer noted down. The balloon is then removed from the bath, and detached when it is cooled.

The temperature  $T$  of the mercurial thermometer requires a correction, which becomes of great importance in high temperatures, and which is owing to the circumstance that a considerable portion of the mercurial column, not being plunged into the bath, remains at a very low temperature. Let  $t$  be the temperature indicated by a small thermometer, the bulb of which is kept in contact with the tube of the principal thermometer, at the height of about one-half of the mercurial column which rises above the level of the bath;

and  $\theta$  the division of the principal thermometer, at about 2 or 3 centimetres above the level of the bath: it may then be admitted that  $(T-\theta)$  represents the portion of the mercurial column at the average temperature  $t$ . Now, this portion would dilate by  $(T-\theta) \cdot \frac{T-t}{6380}$ , if it were heated from  $t$  to  $T$ ; for which reason the true temperature  $T'$  of the bath is obtained by adding to the temperature observed  $T$  the number of degrees represented by the expression  $(T-\theta) \cdot \frac{T-t}{6380}$ .

But as the temperature  $T'$  is that of the mercurial thermometer, it is necessary to find the temperature  $T''$  which corresponds to it on the air thermometer. Mercurial thermometers agree necessarily from  $32^\circ$  to  $212^\circ$ , which are the fixed points by which their scales are governed; while they differ at a temperature above  $212^\circ$ , because the various kinds of glass of which the bulbs of thermometers are made do not obey the same law of expansion. The following table shows the simultaneous temperatures indicated, 1st, by a mercurial thermometer, of which the bulb is made of the ordinary glass used in Paris for making chemical tubes; 2dly, by a mercurial thermometer, of which the bulb is of crystal from Choisy-le-Roi; and 3dly, by an air thermometer, of which the volume of air is constant and the pressure variable.\*

*Simultaneous Temperatures*

Of a mercurial thermometer of ordinary glass.	Of a mercurial thermometer of crystal.	Of an air-thermometer.
100° centigrade	100° .....	100°
109.98 .....	110.05 .....	110
119.95 .....	120.12 .....	120
129.91 .....	130.20 .....	130
139.85 .....	140.29 .....	140
149.80 .....	150.40 .....	150
159.74 .....	160.52 .....	160
169.68 .....	170.65 .....	170
179.63 .....	180.80 .....	180
189.65 .....	191.01 .....	190
199.70 .....	201.25 .....	200
209.75 .....	211.53 .....	210
219.80 .....	221.82 .....	220
229.85 .....	232.16 .....	230
239.90 .....	242.55 .....	240
250.05 .....	253.00 .....	250
260.20 .....	263.44 .....	260
270.38 .....	273.90 .....	270
280.52 .....	284.48 .....	280
290.80 .....	295.10 .....	290

\* This being a merely comparative table, the centigrade divisions have not been corrected to the corresponding temperatures of the Fahrenheit scale.—*W. L. F.*

Of a mercurial thermometer of ordinary glass.	Of a mercurial thermometer of crystal.	Of an air thermometer.
301.08° .....	305.72 .....	300
311.45 .....	316.45 .....	310
321.80 .....	327.25 .....	320
332.40 .....	338.22 .....	330
343.00 .....	349.30 .....	340
354.00 .....	360.50 .....	350

When the operation is performed at higher temperatures, above 570° (Fahrenheit) for example, and great exactness is required, it is better to substitute an air for a mercurial thermometer; which is absolutely necessary when 660° is exceeded, since at this temperature mercury boils under the ordinary pressure of the atmosphere; and the boiling manifests itself even at somewhat lower temperatures in thermometers perfectly freed from air, unless the calibre of the tube be so small as to present great resistance to the ascent of the metal. In a note,\* at the bottom of this page, we shall explain

\* The air thermometer used in these experiments consists of a simple cylindrical glass reservoir, of about 2 centimetres in diameter and 12 or 15 centimetres in length, and terminating by a capillary tube, of which the calibre is 1 or 2 millimetres, and which is bent to a right angle, and drawn out at its end. The reservoir *ab* is kept in the bath, alongside of the balloon in which the vapour is to be generated. The first step is to perfectly dry the reservoir *ab*, by creating a vacuum in it several times, and allowing air to enter which has been dried, by passing through a tube filled with pumice-stone soaked in concentrated sulphuric acid; after which the bath is heated, and, when the temperature becomes stationary at the point at which the experiment is to be terminated, the point of the balloon and that of the air thermometer are closed simultaneously, by means of a lamp.

The air reservoir is then placed on the metallic support represented in fig. 636, the stem passing through a cork which closes a tubulure made in the centre of the disk *gh*, while the curved point *cd* enters a small mercurial bath. The extremity of the point being broken with a pincers, the mercury rises in the tube and partly fills the reservoir *ab*, which is surrounded with pounded ice, in order to reduce the temperature of the air it contains to 32°, when the open point is closed with a ball of soft wax. In order to perform this operation easily, without changing the level of the mercury in the vessel A, a small iron spoon *u* is used, soldered to an iron rod *uv*, which slides along a horizontal bar *vs*, itself movable along the vertical foot *st*; the movable rod *vs* being fixed at such a height that the bowl of the spoon, filled with soft wax, is exactly at the height and in the direction of the point *cd*. It is therefore sufficient, in order to close the point, to slide the end *uv* along the horizontal rod *vs*. The mercury in the vessel A is then exactly levelled to the point *i* of a double-pointed screw *ki*; the ice which surrounded the reservoir *ab* is removed, and, when the mercurial column attains the temperature of the surrounding air, the difference of height between the mercury in the reservoir *ab* and the upper point *k* is exactly measured, by means of

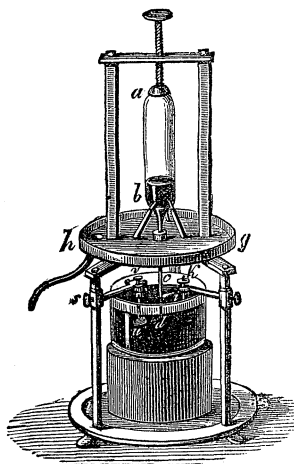


Fig. 636.

the manner of arranging an air thermometer, and deducing the temperature from it.

The balloon A having been well wiped and washed with alcohol,

a cathetometer; and by adding to this difference the length of the screw  $ki$ , the height  $h$  of the column of mercury elevated in the air thermometer is obtained. Let  $h_0$  be this height at  $32^\circ$ ,  $H_0$  the height of the barometer also at  $32^\circ$ , when the point  $d$  is closed with wax; then will  $(H_0 - h_0)$  represent the elastic force of the air in the reservoir  $ab$  at the temperature of  $32^\circ$ . The support is then inverted, the air thermometer removed, after having detached the spoon  $u$ , and it is weighed with the mercury contained: let its weight be represented by  $Q$ . The thermometer is then filled with mercury, which is boiled to drive off the last bubbles of air; the point  $cd$  being kept, during this time, in a small capsule filled with mercury.

When the apparatus is cooled, it is surrounded with melting ice, and completely filled with mercury at  $32^\circ$ ; when it is again weighed, giving now the weight  $Q'$ . The weight  $q$  of the envelope of glass alone being ascertained, after having emptied it of mercury,  $(Q - q)$  is therefore the weight of the mercury at  $32^\circ$ , and  $(Q - q)$  is the weight of the mercury in the thermometer when it was on the support.  $(Q' - Q)$  therefore represents the weight of the mercury at  $32^\circ$ , which occupies the same volume as the air remaining in the thermometer when it is at  $32^\circ$ , and under the pressure  $(H_0 - h_0)$ . If we designate by  $\delta$  the density of the mercury at  $32^\circ$ ,  $\frac{Q - q}{\delta}$  represents the capacity in cubic centimetres of the thermometer, and  $\frac{Q - q}{\delta}$  the volume which the air occupies in this apparatus at the moment of closing the point  $c$  with wax.

Now, the capacity of the thermometer, at the temperature  $T$ , being  $\frac{Q - q}{\delta}$   $(1 + kT)$ , the volume of air  $\frac{Q' - Q}{\delta}$  at  $32^\circ$  and under the pressure  $(H_0 - h_0)$ , therefore occupies, when it is raised to the temperature  $T$ , and under the pressure  $H_0$ , a volume  $\frac{Q' - Q}{\delta} (1 + kT)$ . The volume assumed by a volume of air  $\frac{Q' - Q}{\delta}$  at  $32^\circ$  and under the pressure  $(H_0 - h_0)$ , when raised to the temperature  $T$  and under the pressure  $H'_0$ , may be calculated, by the known laws of the expansion of air, under changes of temperature and pressure; and is thus found to be,

$$\frac{Q' - Q}{\delta} (1 + 0.00367.T) \frac{H_0 - h_0}{H'_0},$$

which leads to the equation,

$$\frac{Q' - Q}{\delta} (1 + 0.00367.T) \frac{H_0 - h_0}{H'_0} = \frac{Q' - q}{\delta} (1 - kT),$$

whence

$$\frac{1 + kT}{1 + 0.00367.T} = \frac{Q' - Q}{Q' - q} \cdot \frac{H_0 - h_0}{H'_0}$$

$T$  may be deduced from this equation, but there is no necessity of knowing its value in order to calculate the density of the vapour, which, in fact, is represented by the expression

$$\frac{P' - P + p}{0.0012932 \cdot V \cdot \frac{1 + kT}{1 + 0.00367.T} \cdot \frac{H'_0}{760}}$$

Substituting for  $\frac{1 + kT}{1 + 0.00367.T}$ , the value first found, there results for the expression of the density of the vapour,

$$\frac{P' - P + p}{0.0012932 \cdot V \cdot \frac{Q' - Q}{Q' - q} \cdot \frac{H_0 - h_0}{760}}.$$

if necessary, its weight  $P'$  is accurately ascertained, taking care to operate as much as possible under the same circumstances of temperature and pressure as were observed in weighing the empty bal-

The process described (§ 1236) is applicable to the determination of the densities of the vapour of all volatile organic substances, and that of volatile mineral substances, when the temperature need not be raised above  $930^{\circ}$ ; but it is of difficult application to higher temperatures, because the glass softens, and the balloon becomes misshapen from the pressure of the metallic bath in which it is heated. By conducting the experiment in the method about to be described, exact results may be obtained even at the temperature of  $1100^{\circ}$  or  $1200^{\circ}$ .

Two tubes  $ab$ ,  $a'b'$ , (fig. 637,) of the same length and diameter, made of as hard glass as possible, are used, one of which serves as an air thermometer, while the second is intended to contain the vapour of the volatile substance. The latter is composed of a reservoir  $a'b'$ , a capillary portion  $b'c'$ , and a larger portion  $c'd'$ , in which a portion of the volatilized substance which escapes from the reservoir  $a'b'$  is condensed; and the air thermometer terminates in a capillary tube  $bc$ , to the end of which is luted a small steel stopcock  $r$ . The two tubes are arranged alongside of each other, on a small support made of three parallel disks of sheet-iron, held

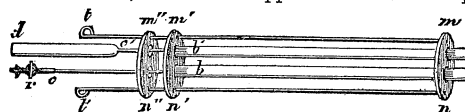


Fig. 637.

together by iron rods. The air thermometer has previously been filled with dry air, and a certain quantity of the substance, the density of the vapour of which is to be determined, has been introduced into the tube  $a'b'c'$ . They are heated simultaneously in air apparatus (fig. 638), made of two or three concentric sheet-iron tubes, closed at

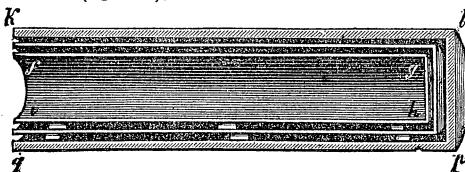


Fig. 638.

one end, and distant from each other about one centimetre, the pipes being introduced into a cast-iron tube ABCD, placed on a semi-cylindrical grate, so that it may be surrounded by charcoal.

The apparatus being arranged, the grate is filled with burning coals, and the temperature rapidly raised, avoiding all cause of sudden cooling. When the volatile substance is distilled, and the excess has condensed in the cold portion of the tube  $c'd'$ , the temperature is again raised, (if the glass does not become misshapen,) this time as slowly as possible. The stopcock  $r$  of the air thermometer is then closed, while at the same time the capillary tube  $b'c'$  which terminates the vapour reservoir  $a'b'$  is sealed by means of the flame of a lamp. The height  $H'$  of the barometer being now noted down, the support, with the two tubes, which are allowed to cool completely, is removed.

In order to determine the temperature  $T$  to which the air thermometer has been raised, the latter is placed in communication with the manometric apparatus, (fig. 639,) which is composed of two tubes  $fg$ ,  $hi$ , luted into a piece having a stopcock  $R$ , resembling that of the figure, the upper end of the tube  $hi$  being open, while the tube  $fg$  is terminated by a bent capillary tube, to which a steel tubulure  $s$  has been luted. Fig. 640 represents a section of the stopcock tubulure  $r$ , mounted on the air thermometer, and a section of the tubulure  $s$  of the manometer. It will be seen that the first tubulure is terminated by a plain surface  $ab$  and a projecting cone  $o$ , while the second has also a plain surface  $a'b'$  and a hollow cone  $o'$ , which exactly fits the plain surface and projecting cone of the other. In order to close them hermetically, it is sufficient to press the two parts against each other, by means of the pincers, (fig. 641,) which is tightened with screws, after having poured in a small quantity of melted caoutchouc.

loon; and in case the new circumstances should differ greatly from the former ones, a correction will be necessary, which, however, we shall not mention, as in general it may be neglected.

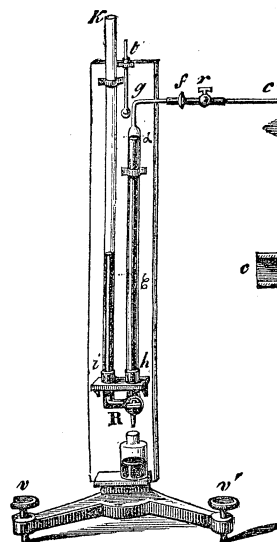


Fig. 639.

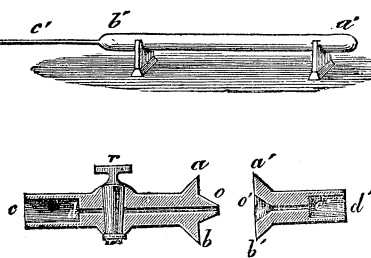


Fig. 640.

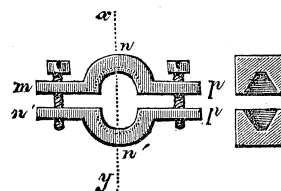


Fig. 641.

The manometer has been filled with mercury before adapting the thermometer to it; and the latter is then completely surrounded by melting ice, when the mercury of the manometer is allowed to escape through the stopcock *R* so as to produce a great difference between the level in the columns *fg*, *hi*. The stopcock *r* is then opened, and a portion of the reservoir *ab* allowed to enter the tube

*gh*, after which mercury is carefully poured into the tube *fi*, so as to bring its level accurately to a mark *a* at the top of the tube *gh*. The next step is to measure, by the cathetometer, the difference *h* of the height of the mercurial columns, and to mark the temperature  $\theta$  of the small thermometer at the side of the manometer, as well as the height *H'* of the barometer. The volume of air is then composed of the volume *V'*, equal to the capacity of the air thermometer *abc*, kept at  $32^\circ$ , and of the volume *v* which the air occupies in the manometer at the temperature  $\theta$ . The weight of this air is

$$0.0012932 \text{ gm. } \left[ V' + v \frac{1}{1+0.00367 \cdot \theta} \right] \frac{H_0 - h_0}{760}.$$

Now the same quantity of air occupied, at the unknown temperature *T*, at the moment of closing the stopcocks, a volume *V'* ( $1+kT$ ), and its weight was expressed by

$$0.0012932 \text{ gm. } \cdot V' \frac{1+kT}{1+0.00367 \cdot T} \cdot \frac{H'_0}{760};$$

so that

$$0.0012932 \left[ V' + v \frac{1}{1+0.00367 \cdot \theta} \right] \frac{H_0 - h_0}{760} = 0.0012932 \cdot V' \frac{1+kT}{1+0.00367 \cdot T} \cdot \frac{H'_0}{760},$$

whence

$$\frac{1+kT}{1+0.00367 \cdot T} = \left[ 1 + \frac{v}{V'} \cdot \frac{1}{1+0.00367 \cdot \theta} \right] \frac{H_0 - h_0}{H'}.$$

The second member of the equation contains only known quantities, except, indeed, the ratio  $\frac{v}{V'}$ , which is determined in the following manner:—The tube *abc* being detached from the manometer, the tube *gh* is completely filled with mercury; and then, bringing the stopcock *R* into the position of fig. 639, the mercury in the leg *gh* is allowed to escape until its level reaches the mark *a*, while the mercury

$P' - (P - p)$  therefore represents the weight of the volatile substance which remains in the balloon, the point of which being broken under the mercury, the atmospheric pressure causes the

which escapes is collected in a small bottle and weighed. Its weight may be considered as representing the volume  $v$ . The mercury is allowed to escape from the leg  $gh$ , it until its level reaches another mark  $\beta$ , on the tube  $gh$ , when the quantity thus obtained, being weighed, compounds to a volume  $v'$  which should be a notable fraction of the capacity of the thermometer-tube. This being done, and the level of the mercury reaching the mark  $\alpha$  of the manometer, under the pressure of the atmosphere, the air thermometer is fitted to the manometer, the reservoir  $ab$  being kept at the temperature of the surrounding medium. As the two columns of mercury are on a level in the manometer, there is a volume of air ( $V + v$ ) under the external pressure  $H$ . The mercury is allowed to flow from the two legs of the manometer, by bringing the stopcock  $R$  into the position in the figure, and the level of the mercury is brought to the mark  $\beta$ ; when the two columns are now no longer on a level, and their difference of height  $h$  can be measured. There is, therefore, a volume of air ( $V + v + v'$ ) under the pressure ( $H - h$ ); and agreeably to the law of Mariotte,

$$\frac{V + v}{V + v + v'} = \frac{H - h}{H},$$

whence the volume  $V$  may be deduced.

It now only remains to ascertain the weight of the vapour which filled the reservoir  $a'b'$  at the moment of closing it, and the capacity of the reservoir. It may be admitted that the reservoir  $a'b'$  does not contain any air, because there was originally introduced into it a quantity of volatile matter sufficient to expel all the air. The closed end of the tube is, therefore, broken, and the latter weighed filled with air and the substance it contains; after which its weight is again ascertained when the substance has been removed, the difference of weight  $\pi$  representing the weight of the substance. In order to obtain the volume  $V$  of the reservoir, the quantity of water which will fill it is weighed; and now all the elements are known which are necessary to calculate the density of the vapour, by means of the formula

$$0.0012932 \cdot V \cdot \frac{\pi}{1 + 0.00367 \cdot T} \cdot \frac{H_0}{760},$$

the value ascertained by the air thermometer being substituted for  $\frac{1 + \lambda T}{1 + 0.00367 \cdot T}$ .

It frequently happens that the substance, the density of whose vapour is to be determined, is changed by absorbing oxygen from the air at the high temperature at which it volatilizes; in which case it becomes necessary to fill the tube  $a'b'$  with nitrogen gas, and further, in order to prevent the air from entering freely, to fit a pointed tube by means of a cork to the tube  $c'd'$ .

By means of the process just described, the density of any vapour might be determined at very high temperatures, if it were possible to procure glass tubes of sufficient hardness; but, unfortunately, the strongest glass softens at a red-heat, and, therefore, cannot be used for higher temperatures. Porcelain tubes, however, made of the same shape as the glass tubes, by the process described in § 715, might answer the purpose. It is, moreover, unnecessary to hermetically seal the fine point  $c'd'$ , when the substance boils at a very high temperature, because there is then no fear, at the moment of withdrawing the tubes from the cylinders, that a portion of the vapours which escape from the reservoir might re-enter the latter.

But there are volatile substances, the density of the vapour of which it would be very interesting to know, and which, at a high temperature, attack the alkaline silicates; in which case tubes of glass or porcelain can no longer be used, and resort must be then had to metallic tubes, previously filled with nitrogen gas. The portion of the volatile substance which remains in the reservoir intended to contain the vapour is then determined by chemical processes.

liquid to ascend, and completely fill the balloon, if the air has been entirely driven out by the vapour, as we shall suppose to be the case. The balloon is then inverted, when the volatile substance, if it is liquid, ascends in the neck, and may be removed with a pipette. The balloon is filled with mercury, which is afterward measured by being poured into a large bell-glass divided into cubic centimetres; by which means the capacity  $V$  of the balloon, at the ordinary temperature  $t$ , is exactly found. If  $k$  represents the coefficient of the average expansion of glass, between the temperature  $t$  and  $T$ , the capacity of the balloon will be  $V(1+kT)$  at the temperature  $T$ . The volume  $V(1+kT)$  of vapour of the volatile substance, at the temperature  $T$  and under the pressure  $H'_o$ , therefore weighs  $(P'-P+p)$ , while the weight of an equal volume of atmospheric air, under the same circumstances of temperature and pressure, is

$$0.0012932 \text{ gm. } V(1+kT) \frac{1}{1+0.00367.T} \cdot \frac{H'_o}{760}.$$

Thus the density of the vapour of the substance is represented by

$$\frac{P'-P+p}{0.0012932 \cdot V(1+kT) \cdot \frac{1}{1+0.00367.T} \cdot \frac{H'_o}{760}}.$$

We have supposed that the vapour had entirely expelled the air from the balloon, and consequently that the latter was entirely filled with mercury; which, however, is rarely the case, as most frequently a bubble of air remains, and sometimes the remaining volume of air amounts to even more than that, when the vapour is very dense, and a large quantity of material has not been originally introduced into the balloon. The experiment does not fail on this account, for it is sufficient to collect this volume  $v$  of air in a small graduated bell-glass, and to measure it exactly. This volume  $v$  weighs

$$0.0012932 \text{ gm. } v \frac{1}{1+0.00367.v''} \cdot \frac{H''_o}{760} = p',$$

$t''$  and  $H''_o$  representing the surrounding temperature and pressure of the air at the moment of measuring the volume  $v$ .

The weight of vapour in the balloon, at the moment of closing it, is therefore  $(P'-P+p-p')$ .

The volume  $v$  of air occupies in the balloon, at the moment of closing it, at the temperature  $T$ , and supposed to be reduced to the pressure  $H'_o$ , a volume

$$v' = v \frac{1+0.00367.T}{1+0.00367.v''} \cdot \frac{H'_o}{H''_o}.$$

The volume occupied by the vapour in the balloon, at the temperature  $T$  and under the pressure  $H'_o$ , is therefore only  $[V(1+kT)-v']$ ; and as an equal volume of air, under the same circumstances of temperature and pressure, weighs

$$0.001293 \text{ gm. } [V(1+kT) - v'] \frac{1}{1+0.00367.T} \cdot \frac{H'_o}{760},$$



the density of the vapour is therefore

$$\frac{P' - P + p - p'}{0.0012932 \left[ V(1 + kT) - v' \right] \frac{1}{1 + 0.00367T} \cdot \frac{H^\circ}{760}}.$$

In accurate experiments, care must be taken to leave but a very small quantity of air in the balloon, in order as much as possible to avoid corrections, which always possess some degree of uncertainty.

The average coefficient  $k$  of the expansion of glass, between the temperatures 0 and  $T$ , varies with the different kinds of glass; and varies, moreover, in the same glass, with the temperature  $T$ . We subjoin its value, at different intervals of temperature, for the ordinary glass of which the balloons used in Parisian laboratories are made:

Between 0° and 100° .....	$k=0.0000276$
“ 150 .....	0.0000284
“ 200 .....	0.0000291
“ 250 .....	0.0000298
“ 300 .....	0.0000306
“ 350 .....	0.0000313

Organic substances which boil at high temperatures are frequently easily altered by the air, at the temperature to which their vapours must be heated in order to obtain constant densities; in which case, care must be taken to fill the balloon with carbonic acid gas, when it is placed in the kettle, before heating the latter. For this purpose, the point of the balloon is made to communicate with a small air-pump, to the second tubulure of which an apparatus disengaging carbonic acid gas is adapted; and a vacuum being made several times, and carbonic acid gas allowed to enter each time, the rest of the experiment is then conducted as usual.

In many cases it may be of advantage to determine the density of a vapour under a pressure below that of the atmosphere, because then the substance boils at a lower temperature, and in general it is not necessary to raise the temperature so high in order to obtain constant densities. This result is particularly advantageous when substances easily altered by heat are operated on, and the boiling point of which is high. In this case, a capillary tube  $ab$ , terminating in a larger one  $cd$ , is soldered to the balloon, (fig. 642;) and the latter being placed in the bath, the tube  $cd$  is made to communicate with a large bottle placed in a water-bath kept at a constant temperature, approaching that of the surrounding temperature; while the second tubulure of the bottle is made to communicate with a mercurial manometer which indicates the internal pressure at every moment, and with an air-pump, by means of which the air in the bottle and balloon is reduced to the desired

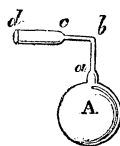


Fig. 642.

degree of elasticity. The experiment is then conducted in the same manner as when the operation is performed under the pressure of the atmosphere; it being sufficient to substitute in the formula the elastic force of the air observed on the manometer, for the barometric pressure  $H'$ .

The second method, which has just been described, to determine the densities of vapours of volatile substances, may furnish very inaccurate results when it is applied to very impure substances, for example, to those containing a small quantity of less volatile matter, the density of whose vapour is very different from that of the substance being examined. The error increases with the quantity of the substance introduced into the balloon, because the less volatile matter is necessarily concentrated in it, and the vapour finally filling the balloon contains a much larger proportion of the foreign matter than the substance which was introduced into it. It is necessary, whenever any doubt may be entertained as to the purity of the substance, the density of whose vapour is to be determined by this method, to carefully collect the portion of matter which remains in the balloon, and subject it to analysis, in order to ascertain if its composition differs appreciably from that of the original substance.

§ 1237. It still remains to explain the method of comparing the density of vapour afforded by experiment with the theoretical density calculated from the formula, when the latter is determined. We will take alcohol as an example.

The experiments detailed (§ 1234) assign 1.602 for the density of the vapour of alcohol, within the limits of temperature in which this vapour obeys the laws of permanent gases. The formula which we have adopted for the equivalent of alcohol is  $C_4H_6O_2$ . Now, as the density of hydrogen is known to be 0.0692, and 2 volumes have been adopted as its gaseous equivalent, the 6 equivs. of hydrogen are therefore represented by 12 volumes of this gas, which weigh  $12 \times 0.0692 = 0.8304$ .

The *hypothetic* density of the vapour of carbon being 0.8290, (§ 203,) and its gaseous equivalent being represented by 1 vol., the 4 equivs. of carbon are therefore represented by 4 vols. of vapour of carbon, which weigh  $4 \times 0.8290 = 3.3160$ .

The density of oxygen gas is 1.1056, and its equivalent is represented by 1 vol.; and 2 equivs. of oxygen are therefore represented by  $2 \times 1.1056 = 2.2112$ .

The formula  $C_4H_6O_2$  therefore gives

4 eq. of carbon.....	3.3160
6 “ hydrogen .....	0.8304
2 “ oxygen .....	2.2112
	<hr/>
	6.3576

Now, since  $\frac{6.3576}{4} = 1.5894$  differs but little from the number 1.602,  
VOL. II.—2L

which has been found by direct experiment, the conclusion may be drawn that the equivalent  $C_4H_6O_2$  of alcohol is represented by 4 volumes of vapour.

The difference between the theoretical number 1.5894 and the number 1.602 found by experiment, may be partly attributed to slight errors which always occur in determinations of this kind; and similar, and even greater differences are observed, when the experiments are conducted with the greatest exactness. This is owing to the fact that the laws of elasticity of gases, and their expansion by heat, which we have admitted as being strictly the same for all the gases above taken into account, are not really so under the circumstances accessible to our means of observation. The gases which have not yet been liquefied differ from it themselves very widely, at the ordinary temperature; and it is, therefore, very probable that the differences are greater for the majority of vapours, even under the most favourable circumstances of temperature and pressure.

#### OF THE ANALYSIS OF GASES.

§ 1238. We have frequently had occasion to refer to the analysis of gaseous substances in the first part of this work, either for the sake of determining the composition of definite gases, or the proportions in which such gases existed in mixtures. We have described the most simple processes used by chemists, but as the processes do not afford the degree of precision demanded by the subject, we shall now describe other processes by which a precision can be attained, in the analysis of gases, which is not exceeded by any of the most exact manipulations of chemical analysis. We shall, in the first place, suppose that it is required to analyze a mixture of atmospheric air and carbonic acid; and, while applying the processes already described, we shall discuss the causes of error to which they are subject.

It will be recollected that a certain volume of this mixture is measured over mercury in a graduated cylinder, and that in order to be more certain of the degree of moisture of the gas, the latter was saturated with moisture by leaving the sides of the cylinder slightly damp.

The first difficulty which presents itself is, What is the temperature of the gas, and what its elastic force? The temperature of the gas is generally assumed as that indicated by a thermometer placed in the vicinity of the cylinder; but is it always certain that the two temperatures are identical? As to the pressure, it is generally reduced to an equality with that of the atmosphere, by properly sinking the cylinder into the mercury-bath; a process which possesses but little accuracy; or, indeed, when the operation is effected more exactly, a certain column of mercury is left upraised, and measured by a graduated scale, or better still, by the process described in the note to page 414.

In order to absorb the carbonic acid, a small quantity of a concentrated solution of caustic potassa is introduced into the bell-glass, and the latter is shaken; after which the proportion of carbonic acid is determined by again measuring the gaseous volume. But the second measuring is still more uncertain than the first, for, to the difficulties already pointed out, is added that of ascertaining the degree of moisture of the gas in the presence of the solution of potassa; in addition to which, the form of the meniscus of the liquid is now changed from convex to concave; and the sides of the bell-glass are moistened with a viscous liquid, which diminishes appreciably its diameter.

These difficulties are overcome by replacing the solution of potassa by a small ball of potassa affixed to a platinum wire, by which it is introduced into the bell-glass through the mercury; but in this case the carbonic acid is very slowly absorbed, which renders it neces-

sary to wait, not only until the absorption of carbonic acid is complete, but also until the potassa has absorbed all the vapour of water which existed in the gas or on the sides of the bell-glass; because it would otherwise be impossible to ascertain its state of saturation. In order to be sure that this condition is fulfilled, the gas must be exactly measured after having with-

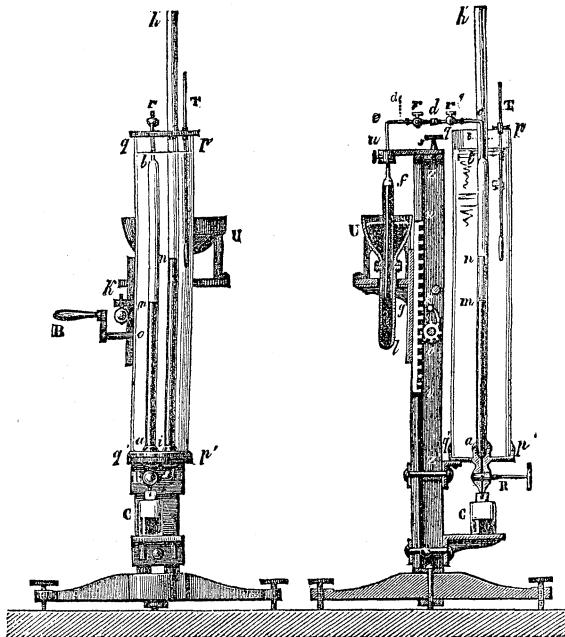


Fig. 643.

Fig. 644.

drawn the ball of potassa, and the latter must be again introduced and allowed to remain for at least 12 hours; when the result of a second measurement of the gas should be identical with the first.

The proportion of oxygen in the remaining gas is determined, either from the gaseous volume which disappears when this gas is burned with an excess of hydrogen, or by the diminution of a volume of the gas when left for a sufficient length of time in con-

tact with a substance which combines with oxygen. The manner of effecting this absorption by phosphorus has already been explained, (§ 946;) and in § 83 the eudiometer in which the analysis is made by combustion was described; but the process is always liable, without regard to the method adopted, to some of the causes of error pointed out above.

§ 1239. With the eudiometric apparatus about to be described

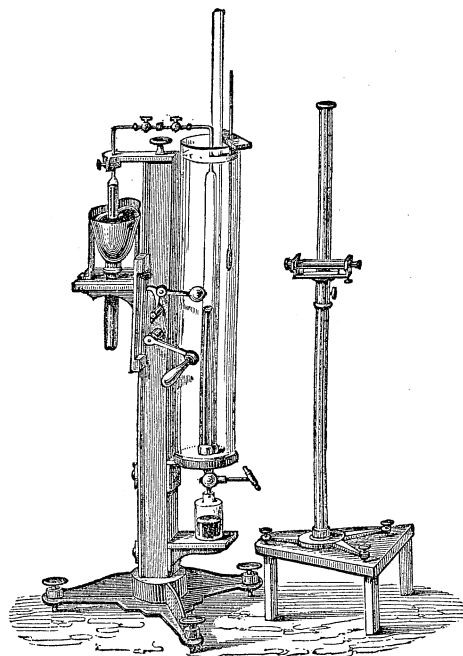


Fig. 645.

these analyses can, on the other hand, be performed very rapidly, and without any danger of the uncertainties just mentioned. Fig. 643 represents the geometrical projection of the anterior surface, and fig. 644 gives a vertical section made through a plane perpendicular to this face; while lastly, fig. 645 shows a perspective view of the whole.

The apparatus is composed of two parts, which may be separated and united at pleasure; and, while the first, or the *measurer*, serves to measure the gas under given conditions of temperature and moisture, in the second the gas is subjected to various absorbent reagents, on which account

we shall call it the *absorption-tube*.

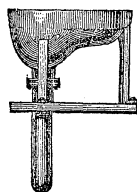
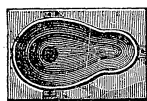
The measurer is composed of a tube *ab* of 15 to 20 millimetres diameter internally, divided into millimetres, and terminating above by a curved capillary tube *bc*, while the lower end is luted into a cast-iron piece *p'q'*, having two tubulures *a*, *i*, and a stopcock *R*. To the second tubulure *i* is luted a straight tube *ih*, open at both ends, of the same diameter as the tube *ab*, and also divided into millimetres. The stopcock *R* has three openings, and resembles precisely that of which sections are seen in figs. 624, 625, and 626, in the three principal positions in which the key may be turned. A communication can therefore be established at will between the tubes *ab*, *ih*, or one or other of these tubes only may be opened to the external air.

The two vertical tubes and the cast-iron piece form a manometric

apparatus contained in a glass cylinder  $pqp'q'$  filled with water, which is maintained at a constant temperature, marked by the thermometer T, during the whole time of the analysis. The manometric apparatus is fixed on a cast-iron stand ZZ' furnished with adjusting screws.

The absorption-tube is composed of a bell-glass  $gf$ , open at the bottom, and terminated above by a curved capillary tube  $fer$ . The bell-glass dips into a small mercurial bath U, of cast-iron, exactly represented in figs. 646 and 647; while the basin U is fixed on a

Fig. 646. plate which can be raised at will along the vertical support ZZ', by means of the toothed rack  $vw$ , which works with the toothed pinion  $o$  set in motion by the crank B. The ratchet  $r$  arrests the toothed-racks and consequently keeps the basin U in any given position. A counterpoise affixed to the ratchet facilitates its working, and, as it is turned to one side or the other, the ratchet is thrown in or out of gear with the pinion.



The ends of the capillary tubes which terminate the absorption-tube and measurer are luted to two small steel stopcocks  $r, r'$ , the ends of which exactly fit each other, and which have the same shape as those represented in fig. 639, sections of which are seen in figs. 640 and 641.

The absorption-tube is maintained in a vertical position by means of pincers  $u$  lined with cork, which are easily opened or closed when the tube is to be removed or replaced. The measurer  $ab$  is traversed at  $b$  by two platinum wires opposite to each other, the ends of which approach to the distance of a few millimetres from the inside of the bell-glass, and of which the other ends are fastened with wax to the lower edge of the large cylinder. The electric spark is passed into the bell-glass by means of these wires; and the water in the cylinder is no obstacle if the spark be furnished by a Leyden jar.

§ 1240. Let us suppose that in this apparatus a mixture of atmospheric air and carbonic acid is to be analyzed.

Through the tube  $ih$  the measure  $ab$  is filled with mercury, until the latter escapes through the stopcock  $r$ , which is then closed; and at the same time the absorption-tube  $gf$  is filled with mercury; to effect which the tube  $gf$  is detached from the pincers  $u$ , and plunged into the bath U, the stopcock  $r$  being open; and the operator sucks with a glass tube furnished with a caoutchouc tubulure, the edge of which is applied to the plane part of the tubulure  $r$ . When the mercury begins to escape, the stopcock  $r$  is closed.

The gas to be analyzed, which has been collected under a small bell-glass, is then introduced into the absorption-tube, and the extravasation is easily performed in the bath U, on account of the shape

given to the latter. The absorption-tube being then replaced by the pincers *u*, the two tubulures *r*, *r'* are fitted to each other: then, elevating one end of the bath U, and allowing the mercury of the measurer to flow from the other through the cock R, and lastly, opening the stopcocks *r*, *r'*, the gas is caused to pass from the absorption-tube into the measurer. When the mercury begins to rise in the capillary tube *fe*, its escape through the stopcock R is slackened, so as to cause the mercury to rise very gently in the tube *fer*, and the cock *r* is closed when the mercurial column reaches a mark *a*, on the horizontal leg *er*, at a small distance from the tubulure *r*. The level of the mercury is then brought to a given division *m* of the tube *ab*, and the difference in height of the two columns can immediately be read on the scale of the tube *ih*. The water in the cylinder has been several times agitated, throughout, by blowing air into it by means of a tube which descends to the bottom.

Let *t* be the temperature of the water, which is to be stationary during the analysis, *f* the elastic force of the aqueous vapour saturated at this temperature, *V* the volume of the gas, *H* the height of the barometer, and lastly, *h* the height of the mercury elevated: then will  $H + h - f$  be the elastic force of the gas when supposed dry. The temperature of the water in the cylinder should be nearly that of the surrounding air, which does not vary sensibly during the short duration of the experiment; and it is therefore unnecessary to reduce to 32°, by calculation, the height of the barometer, and that of the mercury elevated in the manometric apparatus *abih*. The gas collected in the measurer is moreover always saturated with moisture, because the sides of the tube *ab* are moistened with a small quantity of water; and this is constantly the same, since it is that which the mercury does not remove when the tube is filled with it.

When this is done, the mercury is again allowed to flow through the stopcock R, and the cock *r* is opened in order to allow all the gas as well as a column of mercury to pass into the tube *rcb*, after which the stopcock *r'* is closed. The absorption-tube is then detached; and a drop of a concentrated solution of potassa is passed up by means of a curved pipette; when the absorption-tube is again fitted to the measurer, and the bath U allowed to fall to its full extent; and then, after having poured a large quantity of mercury into the tube *hi*, the stopcocks *r*, *r'* are successively opened. The gas thus passes from the measurer into the absorption-tube, and the small quantity of solution of potassa completely moistens the sides of the bell-glass. The cock *r* is closed when the mercury begins to fall in from the measurer into the vertical leg *ef* of the absorption-tube; and after waiting for a few moments, in order to give time for the absorbing action of the potassa, the gas is passed from the absorption-tube back into the measurer, by causing the bath U to ascend, and the mercury to flow through the cock R. As soon as

the alkaline solution begins to rise in the tube  $fe$ , an inverse movement is caused by closing the stopcock  $r$ ; that is, the gas is again passed from the measurer into the absorption-tube, by lowering the bath  $U$ , and again pouring mercury into the tube  $ih$ . The intention of this operation is to again moisten the sides of the bell-glass  $fg$  with the solution of potassa, and subject the gas to the absorbing action of the new layer of potassa.

If it be deemed necessary, these operations may be repeated several times; although, after the second, the whole of the carbonic acid is generally absorbed. The gas is then passed for the last time from the absorption-tube into the measurer, and the cock  $r$  is closed when the top of the alkaline column reaches the mark  $a$ . The level of the mercury in the tube  $ab$  being brought to  $m$ , the difference of height  $h'$  of the mercury in the two legs  $ab$  and  $ih$  is measured, and the height  $H'$  of the barometer is noted down. We shall suppose that the temperature of the water in the cylinder has not changed: if otherwise, it must be restored to the temperature  $t$ , by the addition of hot or cold water.

The elastic force of the gas, dry and deprived of carbonic acid, is therefore  $(H' + h' - f)$ ; and consequently  $(H + h - f) - (H' + h' - f) = H - H' + h - h'$  is the diminution of elastic force caused by the absorption of the carbonic acid; and  $\frac{H - H' + h - h'}{H + h - f}$  represents the proportion of carbonic acid in the gas when supposed dry.

§ 1241. The proportion of oxygen which exists in the gas remaining must now be determined; for which purpose the absorption-tube is detached and washed several times with water. It is dried, first with tissue-paper, and then by bringing it into combination with an air-pump; and lastly, after having filled it with mercury, it is fitted to the measurer. The bath  $U$  being raised as high as possible, the mercury is allowed to run through the stopcock  $R$ : then, opening carefully the cocks  $r$  and  $r'$ , the mercury of the absorption-tube is passed into the tube  $ar'$  of the measurer, taking care to close the cock  $r'$  when the extremity of the mercurial column reaches a second mark  $\phi$  on the vertical leg  $bc$ . The mercury in the measurer is again brought to the level  $m$ , and the difference of level  $h''$  and the height  $H''$  of the barometer is ascertained.  $H'' + h'' - f$  is therefore the elastic force of the dry gas, the quantity of which is somewhat smaller than in the measure made immediately after the absorption of the carbonic acid, because a small quantity (about  $\frac{1}{3000}$ ) has been lost by detaching the absorption-tube from the measurer. This small loss does not affect the result of the analysis, because the gas is again measured.

The absorption-tube being once more detached from the measurer, the hydrogen gas intended to burn the oxygen is now introduced into the latter by arresting the ascending mercury at the mark  $\phi$ . The mercury is again levelled to  $m$ , the difference of height  $h'''$  of



the two columns of mercury measured, and the height  $H'''$  of the barometer observed.  $H''' + h''' - f$  is therefore the elastic force of the mixture of hydrogen and oxygen to be analyzed. As some time is required for the perfect admixture of the gases, combustion by the electric spark cannot be immediately effected. The gas must again be passed from the measurer into the absorption-tube, and a small quantity of mercury, which produces an agitation in the gas, allowed to flow through the tube  $cdef$ ; and lastly, the mixture is passed back into the measurer, this time allowing the mercury to entirely fill the tube  $r'cb$ , in order that the whole volume of gas may be subjected to combustion.

The electric spark is then applied, and after having established an excess of pressure in the measurer  $ab$ , the stopcocks  $r, r'$  are carefully opened, in order to allow the mercurial column to retrograde into the tube  $bc r'$ ; and it is stopped when it reaches the mark  $e$ . The elastic force of the gas remaining is again measured, after having levelled the mercury to  $m$ ; and  $H'''' + h'''' - f$  is then the elastic force. Consequently,

$(H''' + h''' - f) - (H'''' + h'''' - f) = H''' - H'''' + h''' - h''''$  is the elastic force of the gaseous mixture which disappeared during combustion;

$\frac{1}{3}(H''' - H'''' + h''' - h'')''$  is the elastic force of the oxygen contained in the dry gas, of which the elastic force is  $(H'' + h'' - f)$ , and  $\frac{1}{3} \frac{H''' - H'''' + h''' - h''''}{H'' + h'' - f}$  is the proportion of oxygen contained in the gas, when freed from carbonic acid; whence the proportion of oxygen in the original mixture may be easily deduced.

§ 1242. The example chosen shows the mode of operating with the apparatus: the manipulations are of such a simple character, that the operator requires no assistant; and lastly, the operation is so rapid, that less than three quarters of an hour is required for that just described; the greater portion of which time is consumed by the absorption of the carbonic acid and the cleansing of the bell-glass after the experiment. Air, freed from carbonic acid, can be analyzed in less than 20 minutes.

We will remark, that in this manner of operating, there is no necessity of any gauging capacity, which is always a very delicate operation; but as the volume of the gas is constantly the same, only its elastic force, after each operation, is determined. It is generally sufficient to measure the elastic forces of the gas by reading directly on the graduated tubes  $ab, ih$ , the divisions to which the columns of mercury correspond; but in order to avoid errors of parallax, the divisions are read by means of a horizontal glass, (fig. 645,) thus allowing no error greater than  $\frac{1}{10}$  of a millimetre. Although this is sufficiently precise, the cathetometer furnishes a still greater degree of accuracy.

The same apparatus may also be used in another way; and in-

stead of maintaining the volume of gas constant, and measuring its elastic forces, the inverse may be done, by making the elastic force constant and measuring the volume. In this case, the tube *ab* should be accurately gauged, for which purpose it is sufficient to fill the measure accurately with mercury; then keeping the temperature of the surrounding water constant, the mercury is allowed gradually to escape by bringing the stopcock R into the position necessary for the escape of the metal in the tube *c* alone. The mercury which runs out is weighed, and the division on the scale of the tube, reached by the level of the mercury, each time, is marked.

§ 1243. The analysis of gases by combustion is exact only when the ignifiable and combustible gases exist between certain limits. When the detonating mixture forms only a small portion of the total volume, it is no longer inflamed by the passage of the electric spark, or, at least, the combustion is but partial. Experiment has shown that, in mixtures of hydrogen and oxygen in which the hydrogen is in excess, there is no combustion when the detonating mixture forms a less fraction than 0.08 of the whole gas; and when it exceeds this, the inflammation and combustion are complete.

The limits differ when oxygen predominates in the mixture: combustion is complete as long as the volume of the detonating mixture does not form a less fraction than 0.17 of the whole gas; but when this fraction is included between 0.17 and 0.10, the combustion is only partial; and lastly, below this there is no inflammation. The presence of an excess of oxygen therefore opposes the combustion of the mixture more powerfully than an excess of hydrogen. Whatever, moreover, may be the excess of oxygen in the mixture, there is no fear of a portion of this gas disappearing from combining with the mercury.

By operating on mixtures of various proportions of carbonic acid and detonating gas, (2 volumes of hydrogen, 1 of oxygen,) it is easy to ascertain that carbonic acid prevents the combustion of the detonating mixture more effectually than oxygen.

If the mixture contains, at the same time, nitrogen, oxygen, and hydrogen, the oxygen predominating over the hydrogen, the analysis may be inaccurate, because subnitrate of mercury is formed. But during the formation of this substance, a high temperature must be developed at the moment of combustion, producing a copious volatilization of mercury, and this condition is fulfilled only when the volume of the detonating mixture is at least 0.8 of the gas which remains after explosion, or 0.45 of the whole volume.\*

These limits of explosibility vary sensibly with the diameters of

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\* Bunsen gives as the best proportion 30.0 volumes of combustible gas to 187.3 volumes of nitrogen and 41.0 volumes of oxygen, which ratio may easily be obtained by the admission of atmospheric air, oxygen, or hydrogen. My own experience also proves the above proportion to be the safest.—*W. L. F.*

the eudiometric tubes; and the variations are particularly observable in mixtures of detonating gas and carbonic acid.

In exploding a mixture of hydrogen, carbonic acid, and oxygen or atmospheric air, the hydrogen being in excess, *a portion of the carbonic acid is always converted into carbonic oxide*, for which reason this gas must be first absorbed by potassa, when the proportion of oxygen in a mixture of gases containing carbonic acid is to be determined by combustion.

Reciprocally, when operating with a detonating mixture containing an excess of hydrogen and some carbonic oxide, *a quantity of the latter gas in proportion to the excess of oxide of carbon over hydrogen, is always converted into carbonic acid*.

#### *Use of Absorbing Reagents.*

§ 1244. Absorbing reagents may often be advantageously used in the analysis of gaseous mixtures. The use of the solution of potassa for the absorption of carbonic acid having been previously (§ 1240) explained, we will now review the reagents which may be used for the absorption of oxygen.

Phosphorus absorbs oxygen very slowly at a low temperature, the absorption being often still incomplete after several days; and toward the close, in order to hasten it, the tube should be placed in the sun. When a ball of phosphorus has been introduced into a gas deprived of oxygen, and contained in a bell-glass of which the sides are moistened by an alkaline solution, the gas is constantly observed to increase in volume, probably owing to the fact that by the contact of the phosphorus with the alkaline solution, hypophosphite of potassa is formed, and hydrogen or phosphuretted hydrogen is evolved; which must be carefully avoided in analyses.

The alkaline sulphides, sulphites, and hyposulphites absorb oxygen so slowly that it is impossible to employ them in analysis; for it becomes necessary to use a considerable quantity of the absorbent liquid; and if this be allowed to act for an indefinite length of time, an absorption greater than that corresponding to the oxygen contained in the gaseous mixture often ensues.

Protosulphate of iron saturated with deutoxide of nitrogen absorbs oxygen more rapidly, but does not afford exact results. After the absorption, the gas must be brought into contact with a solution of pure protoxide of iron, in order to absorb the deutoxide of nitrogen which the first liquid may have given off. The gas is therefore brought into contact with considerable volumes of liquid, and it is always to be feared that its composition may be altered by an absorption or evolution of gas effected by these liquids.

Hydrated protoxide of iron, suspended in an alkaline solution, absorbs oxygen rapidly; and in order to use this reagent, several narrow tubes, open at both ends, are first placed in the absorption-tube, and then 1 or 2 cubic centimetres of the liquid are intro-

duced; and when the gas is subsequently passed into the absorption-tube it is exposed to a large absorbing-surface, because the sides of the tube are covered by the hydrated protoxide of iron. The tubes inside may also be dispensed with if only the absorption-tube be shaken frequently after having separated it from the apparatus; but then the viscous liquid frequently produces a large quantity of froth, and requires a long time for settling.

Protochloride of copper dissolved in ammonia, and the ammoniacal protosulphite of copper, also absorb oxygen very rapidly. The tube containing the gas and absorbent liquid must be frequently shaken; but, as the gas then contains necessarily a small quantity of ammoniacal gas given off by the liquid, it becomes necessary, before passing it into the measurer-tube, to collect it in a second absorption-tube containing a few drops of dilute sulphuric acid. Pipettes for gas, such as are represented in fig. 648, may also be

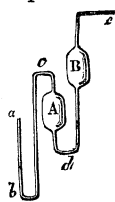


Fig. 648.

used. The bulb A being filled with mercury, and containing the absorbent liquid at its upper part, and the leg *abc* being also filled with mercury, which is easily done by dipping the end *a* into mercury and sucking through the end *o*, the leg *ab* is introduced into the bell-glass containing the gas, and, by sucking through the opening *o*, the gas is made to pass into the bulb A. The leg *abc* being filled with mercury, the apparatus is shaken, so as to cause the absorbing liquid to act on the gas. When the absorption is terminated, the gas is again passed into the absorption-tube, to effect which the end *a* is dipped into the mercury, when, by sucking at *o*, a large quantity of mercury is made to pass into the bulb B, so that the mercurial column is higher in the leg *dBo*; after which the opening *o*, is immediately closed with the finger slightly moistened, and, by introducing the leg *ab* into the absorption-tube, and then gradually and carefully unclosing the opening *o*, all the gas is made to pass back into the absorption-tube by arresting the flow at the moment that the absorbing liquid reaches the extremity *a*. There has been also previously introduced into the absorption-tube a drop of dilute sulphuric acid to absorb the ammonia contained in the gas.

The use of absorbing liquids in the analysis of gases is liable to a source of error which is not always easily avoided. As a considerable volume of it must be used, an alteration of the composition of the gaseous residue by the small quantities of gas which the liquid can dissolve or exhale is to be feared. When it is used only for the analysis of mixtures of oxygen and nitrogen, this error is less to be feared, if care be taken never to introduce into the apparatus any thing but a solution of protochloride of copper which has been for some time exposed to an atmosphere of pure nitrogen; which condition is naturally fulfilled when this liquid is preserved in a well-stoppered bottle which is not opened too frequently, or in

the pipettes (fig. 648) before mentioned. But this would not be the case if the gaseous residue contained other gases besides nitrogen.\*

The analysis of air by absorbent reagents is longer than that by combustion with hydrogen. In order not to be uneasy as to the exactness of the analysis, it is necessary to ascertain that the volume of the gaseous residue is not again diminished by remaining for a long time in contact with the absorbent reagent. Combustion by hydrogen is, on the contrary, always immediately complete, if indeed care has been taken to mix the gases well by passing them twice from the absorption-tube to the measurer, and if the proportion of combustible gas to the mixture exceeds the limit above mentioned, (§ 1243,) which is readily known when the analysis is terminated.

In some special cases, which will subsequently be pointed out, combustion cannot be employed, and absorbing reagents must be resorted to for the determination of the oxygen.

Sulphurous acid gas is absorbed by potassa, and when it is mixed with carbonic acid, the mixture can be analyzed by means of red oxide of mercury or peroxide of lead, which absorb the sulphurous acid alone. For this purpose, the oxides are applied, made into a thick paste with a small quantity of water, to a rod of unglazed porcelain, which is introduced into the absorption-tube containing the gaseous mixture, where it is allowed to remain until the absorption is complete. The separation of the two gases is more readily effected by means of a concentrated solution of bichromate of potassa mixed with sulphuric acid, which absorbs the sulphurous acid alone.

Cyanogen is immediately absorbed by potassa; and may also be absorbed by oxide of mercury suspended in water, but the absorption is very slow.

Sulphydric acid is absorbed by a small quantity of a solution of sulphate of copper or acetate of lead.

Bicarburetted hydrogen is absorbed by Nordhausen sulphuric acid strongly charged with anhydrous sulphuric acid. This solution is prepared by pouring a small quantity of concentrated sulphuric acid into a tube in which anhydrous sulphuric acid has been condensed; and a small quantity of the fuming acid may be introduced, by means of a curved pipette, into the absorption-tube containing the gaseous mixture; but then a considerable quantity of

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\* Since the original was written, a new and excellent method for determining oxygen has been discovered by Liebig. The air to be analyzed is passed into a graduated tube filled with mercury, over a mercury-bath, and after having read off the volumes, without regard to temperature, pressure, or tension, a small quantity of a most concentrated solution of caustic potassa is introduced, and the volume again read off immediately, to ascertain the proportion of carbonic acid. A few drops of pyrogallie acid are then passed into the tube, by which means the oxygen is totally absorbed at once; and the diminution of volume shows directly the proportion of oxygen.—*W. L. F.*

sulphurous acid, arising from the reaction of the mercury on the anhydrous sulphuric acid, is formed. It is better to soak a piece of platinum-sponge or coke fastened to a platinum wire in it, and then introduce it into the gas. In all cases, before passing the gas into the measurer, it is necessary to allow it to remain in a second tube, in contact with an alkaline solution; and it is also essential that the gaseous mixture subjected to the action of fuming sulphuric acid should contain no oxygen; as, by contact with the acid, the mercury might readily absorb a portion of that gas.

The methods by absorption may frequently be advantageously combined with those by combustion in the analysis of gases; but they must be used with great caution, as they can readily lead into error, particularly when the gas to be analyzed exists in very small quantity.

#### APPLICATION OF THESE METHODS TO THE ANALYSIS OF A FEW GASEOUS MIXTURES.

§ 1245. In the following pages we shall explain the application of the methods just described to the analysis of the various gaseous mixtures which may occur; but we shall only consider the mixtures into which oxygen, hydrogen, nitrogen, oxide of carbon, protocarburetted and bicarburetted hydrogen enter, since these are the compounds which most frequently occur. If, in addition, carbonic acid, cyanogen, sulphuric acid, or sulphurous acid, exist in such mixtures, they must first be absorbed by the absorbing reagents mentioned in § 1244.

We shall suppose that the gaseous mixtures have been previously freed from the latter gases, and particularly from carbonic acid.

##### *Mixtures of Oxygen and Nitrogen.*

§ 1246. Mixtures of oxygen and nitrogen are analyzed by combustion in the eudiometer by the process detailed, (§ 1241.) We shall now consider only the two extreme cases:

1st. When the mixture contains very little oxygen.

2dly. When, on the contrary, it contains very little nitrogen.

When the gaseous mixture contains very little oxygen, combustion cannot be effected, or if, after having mixed it with an excess of hydrogen, the electric spark be passed through it, combustion is imperfect. A certain quantity of gas from the battery is then added, and, after having made a homogeneous mixture by passing the gas several times from the measurer to the absorption-tube, the spark is passed through; when combustion is perfectly effected, and the decrease of volume of the mixture gives the sum of the oxygen and hydrogen which combined together,  $\frac{1}{2}$  of which is due to the oxygen, while the hydrogen occupied  $\frac{3}{2}$ . The gas from the battery need not be taken into account, because it disappears totally during combustion. It is, moreover, evident that it must always be ascertained if the volume of hydrogen added is greater than the  $\frac{3}{2}$  of a volume which disappeared; for if it were otherwise, it would be owing to a portion still remaining in the gaseous residue.

In order to prepare gas from the battery, freshly boiled water, to which a small quantity of sulphuric acid has been added, is introduced into a large tube closed at one end; and two slips of platinum foil terminating the wires of the battery, which pass through the cork in the tube, are plunged into the water.

The same tube is traversed by a discharging-tube, by means of which the gases are collected over mercury. Four of Bunsen's elements, moderately charged, are sufficient to afford a copious evolution of gas; and the latter is allowed to permeate the mercury for several hours, in order to be sure that the water has dissolved both gases in proper proportions, under an atmosphere formed of 1 volume of oxygen and 2 volumes of hydrogen. The gas is then collected in bell-glasses, and before using it, an experiment is made to ascertain that it leaves no residue on combustion. For this purpose, a certain volume of atmospheric air being exactly measured in the eudiometer, and a nearly equal volume of gas from the battery introduced and perfectly mixed with the air, the spark is passed through. If the gas from the battery contains the two gases in the exact proportions which form water, the atmospheric air occupies, after combustion, exactly the same volume as before.

When, on the contrary, the mixture contains a large quantity of oxygen, combustion is easily effected, and the analysis is exact, provided there be an excess of hydrogen. But when the approximate composition of the gas is unknown, it is sometimes necessary to add so great a quantity of hydrogen that this quantity can be no longer measured by reducing the gas to the same volume, because the column of mercury which balances it would exceed the upper end of the tube *cd*. This, indeed, might be avoided by operating on a smaller quantity of the gas to be analyzed; but the analysis can be continued by bringing the mixture of gas and hydrogen to a mark *m'* placed lower than the mark *m*. The electric spark is passed after having reduced the gas nearly to an equilibrium with the external pressure, and the elastic force of the residue is measured, either at the level *m*, or the level *m'*. It is easy to determine by calculation, and by the assistance of another measurement with the apparatus, the elastic forces which the gaseous mixture would present, if, instead of reaching the level *m'*, they had constantly remained at *m*. It will frequently happen that the gaseous residue of combustion, levelled successively to the marks *m* and *m'*, corresponds to elastic forces measurable on the tube *ih*; but should it be otherwise, a portion of the gas is allowed to escape, and a small quantity of atmospheric air to enter, in order to fulfil this condition. Let *H'* and *H''* be the elastic forces which correspond to the same gas when it is necessarily levelled to the marks *m* and *m'*; *H* the elastic force of the mixture of gas and hydrogen which, not being able to be levelled at *m*, has reached the mark *m'*; and *x* the elastic force of the gas had it been levelled at *m*: we shall then evidently have

$$x = H \frac{H'}{H''}.$$

The inverse inconvenience frequently occurs when the gaseous residue is too small to be measured at the mark *m*; and it is then measured at a higher mark, and, by a calculation similar to that just made, the elastic force which the gas would present if the level were made at *m* is determined.

The difficulty may also be avoided in another way. After having passed the gaseous residue, of which the volume is too small to be measured, into the absorption-tube at the ordinary mark, a certain quantity of air is introduced into the measurer, the elastic force of which is determined after having levelled the mercury to the marks *m* and *c*; after which the gas collected in the absorption-tube is introduced, and the increase it produces in the elastic force is determined.

If the proportion of nitrogen in the mixture is very small, and if no great excess of hydrogen has been introduced, it may happen that the residue of combustion can only be measured by reducing it to a very small volume; in which case it is proper, if great exactness is required, to regard this analysis merely as approximative, and to mark a new one in which a larger proportion of hydrogen must be used.

#### *Mixture of Hydrogen and Nitrogen.*

§ 1247. In order to analyze this mixture, it is burned in the eudiometer with an excess of oxygen; and the volume of hydrogen is then  $\frac{2}{3}$  of the volume disappeared. In this experiment it is necessary to observe that the volume of the detonating gas does not form more than 0.8 of the gaseous residue which remains

after combustion, as otherwise nitrate of mercury would be formed, (§ 1243.) It is always easy to avoid this accident by increasing the quantity of oxygen,\* of which the greater or less excess does not affect the accuracy of the analysis. The combustion may also be made at two periods, by adding in the first place an insufficient quantity of oxygen, which is exactly measured, passing the spark and measuring the residue; and then adding an excess of oxygen accurately determined, and effecting a new combustion. This method should always be employed when the gas contains but very little nitrogen, because it then becomes necessary to add a great excess of oxygen in order to be able to measure the residue after combustion. It is also practicable to increase the residue, by adding to the mixture to be analyzed atmospheric air accurately measured, and then oxygen, in order to have an excess of the latter gas.

If the proportion of hydrogen, on the contrary, is very small, an inexplusive mixture is obtained after the addition of oxygen, and, in order to effect combustion, gas from the battery must be added.

*Mixture of Oxygen and Hydrogen.*

§ 1248. After having measured the gas in the eudiometer, an electric spark is passed through, when  $\frac{2}{3}$  of the volume disappeared are hydrogen, and  $\frac{1}{3}$  oxygen. As the gaseous residue must be either hydrogen or oxygen, it is sufficient to ascertain its nature. If the residue is too small to be measured, it is necessary, after ascertaining its nature, to make a second analysis after adding to the mixture an excess of one or the other gas exactly measured; or to employ the method described § 1246.

*Mixture of Nitrogen, Oxygen, and Hydrogen.*

§ 1249. This mixture is analyzed like the preceding, with the only difference, that after having effected combustion by the electric spark, and ascertained if hydrogen or oxygen remains in the residue, an excess of the gas wanting is added, and another combustion effected, after the addition of gas from the battery, if it be necessary. The same precautions as in the analysis of the mixture of hydrogen and oxygen are used, care being also taken, that if either of these combustions take place in the presence of an excess of oxygen, the volume of detonating gas shall never form more than 0.8 of the residue after combustion, to prevent the forming of nitric products; which accident may, however, always be avoided by the addition of a certain quantity of atmospheric air, which must then not be omitted in the calculation.

*Mixture of Oxygen and Oxide of Carbon.*

§ 1250. The electric spark being passed through, and the residue being measured, the latter is passed into the absorption-tube, and brought in contact with the solution of potassa, in order to absorb the carbonic acid formed. Now, since 1 volume of oxide of carbon consumes  $\frac{1}{2}$  volume of oxygen, and yields 1 volume of carbonic acid, the volume of oxide of carbon sought is precisely equal to that of the carbonic acid formed; and it is also double of the decrease of volume in the gas by combustion.

If the proportion of oxide of carbon is small, combustion is either imperfect or null, in which case gas from the battery must be added. The addition of this gas is very useful in all cases, because, as the heat developed by the combustion of the oxide of carbon is not very great, combustion is frequently incomplete.

*Mixture of Nitrogen and Oxide of Carbon.*

§ 1251. In the case of this mixture the explosion is effected after adding an excess of oxygen which is exactly measured, and then a certain quantity of gas from the battery; after which the volume of the oxide of carbon is double of that which disappears by combustion, and equal to the volume of carbonic acid formed, which is ascertained exactly by absorbing it by potassa. Care must be taken that the proportion of the combustible mixture to the inert gas be not great enough to form nitric products, which accident is, indeed, only to be feared when a large quantity of gas from the battery has been added, because then the temperature rises sufficiently high to produce a free volatilization of the mercury. It is avoided



in all cases, by adding to the gas a proper quantity of atmospheric air, which must not be neglected in the calculation of the results.

*Mixture of Hydrogen and Oxide of Carbon.*

§ 1252. A volume of oxygen somewhat greater than its own being added to this mixture, the explosion is effected and the absorption  $m$  marked; and lastly, the carbonic acid is absorbed by potassa. Let  $n$  be the proportion of carbonic acid thus found,  $x$  the proportion of hydrogen,  $z$  that of the oxide of carbon. The hydrogen, by burning, consumes half of its volume of oxygen; and thus, in consequence of the combustion of the hydrogen, there is a decrease of volume  $\frac{1}{2}x$ . The oxide of carbon consumes half of its volume of oxygen, and produces a volume of carbonic acid equal to its own; and the absorption produced by the combustion of this gas is therefore  $\frac{1}{2}z$ . Thus we have,

$$\begin{aligned}\frac{1}{2}x + \frac{1}{2}z &= m, \\ z &= n, \\ x &= \frac{2m - n}{3}.\end{aligned}$$

whence

It is necessary to add a considerable volume of oxygen, in order that there shall remain, after explosion, enough gas to allow it to be accurately measured. If the original mixture contained very little hydrogen, it would be prudent, after combustion, to introduce gas from the battery, and effect a new explosion, in order to be sure of completely burning the oxide of carbon.

*Mixture of Nitrogen, Oxygen, and Oxide of Carbon.*

§ 1253. If this mixture contains a large amount of nitrogen, a small quantity of oxide of carbon, and oxygen more than sufficient to convert the oxide of carbon into carbonic acid, gas from the battery is added to the mixture, and an explosion effected. Let  $m$  be the absorption produced by the combustion: the volume  $n$  of carbonic acid formed is then determined. Let  $V$  be the volume of the original mixture,  $y$  the volume of oxygen,  $z$  that of oxide of carbon, and lastly  $u$  that of the nitrogen; there will then result, in the first place, the two equations:

$$\begin{aligned}z &= n, \\ \frac{z}{2} &= m, \quad \text{whence} \quad n = 2m,\end{aligned}$$

which should give the same value for  $z$ ; proving that it was in fact oxide of carbon which existed in the mixture.

An excess of hydrogen is then added, and a certain quantity of gas from the battery if it is probable that but very little oxygen remains in the mixture: let  $m'$  be the new absorption effected by the combustion, and there results,

$$\begin{aligned}y &= \frac{n}{2} + \frac{m'}{3}, \\ u &= V - y - z = V - \frac{3n}{2} - \frac{m'}{3}.\end{aligned}$$

If the oxide of carbon predominates over the oxygen, an excess of oxygen  $a$  must be immediately added, and then the equations are as follows:

$$\begin{aligned}z &= n, \\ z &= 2m, \\ y &= \frac{n}{2} + \frac{m'}{3} - a, \\ u &= V - y - z = V - 3m - \frac{m'}{3} + a.\end{aligned}$$

If the nitrogen existed in small quantity, it would be necessary to add for the first combustion a large quantity of oxygen in case the oxide of carbon should predominate, and, for the second combustion, a large excess of hydrogen, in order to have, after each of these combustions, a gaseous residue sufficient to enable its accurate measurement in the apparatus. If one or the other of these combustions

appear feeble, gas from the battery must be introduced before passing the spark, and it must be ascertained if the volume is altered by this new explosion.

*Mixture of Nitrogen, Oxygen, Hydrogen, and Oxide of Carbon.*

§ 1254. Several cases of this mixture may occur, according as one or the other gas predominates. We shall, in the first place, suppose that the oxygen exists in greater quantity than that necessary to completely burn the hydrogen and oxide of carbon: combustion is immediately effected by the spark, if the combustible mixture forms a considerable proportion of the inert gas; but if otherwise, the spark is passed only after having added the gas from the battery. Let  $m$  be the volume which disappears by the combustion,  $x$  the volume of hydrogen; then, retaining for the other gases the same characters as above, we shall have

$$\frac{3}{2}x + \frac{1}{2}z = m.$$

The carbonic acid is absorbed by potassa, causing a diminution of volume  $n$ , which gives:

$$z = n.$$

An excess of hydrogen being then introduced and the explosion effected, a new absorption  $m'$  is observed, whence

$$y = \frac{m'}{3} + \frac{z}{2} + \frac{x}{2};$$

lastly,

$$u = V - x - y - z;$$

whence follows

$$\begin{aligned} x &= \frac{2m-n}{3}, \\ y &= \frac{m+m'+n}{3}, \\ z &= n, \\ u &= V - \frac{3m+m'+3n}{3}. \end{aligned}$$

The quantity  $u$  can be verified by exploding the last gaseous residue, consisting only of nitrogen and oxygen, with an excess of hydrogen.

If oxygen exists in the mixture in a quantity insufficient to completely burn the hydrogen and oxide of carbon, a certain quantity  $a$  of it is added, and for the moment this new mixture is regarded as that to be analyzed: the equations of the preceding case are consequently applicable, and it is sufficient, at the end of the analysis, to diminish the oxygen  $y$  by the quantity  $a$  which had been added.

Lastly, if the nitrogen be present in very small quantity, the same method could be employed; and it would suffice to add, before each combustion, a sufficiently large excess of the gas which is to effect it, in order that the gaseous residue may be exactly and easily measured in the apparatus. A certain quantity of atmospheric air may also, in this case, be added to the original mixture, which is to be brought into the final calculation.

*Mixture of Oxygen and Protocarburetted Hydrogen.*

§ 1255. If the oxygen does not exist in a quantity more than sufficient to completely burn the protocarburetted hydrogen, a quantity  $a$  of oxygen must be added, which is to be afterward remembered in the calculation. Let  $m$  be the diminution of volume produced by the explosion, and  $n$  that effected by the absorption by potassa.

As 1 volume of protocarburetted hydrogen consumes 2 vols. of oxygen and yields 1 vol. of carbonic acid, we shall have, designating by  $v$  the volume of protocarburetted hydrogen,

$$\begin{aligned} 2v &= m, \\ v &= n, \text{ whence } 2n = m; \end{aligned}$$

which two relations should give the same value for  $v$ , if the gas is protocarburetted hydrogen.

2 m 2

*Mixture of Hydrogen and Protocarburetted Hydrogen.*

§ 1256. To this mixture a large excess of oxygen is added, in order that, after the combustion and absorption of the carbonic acid, there shall remain a volume which can be exactly measured in the apparatus. After passing the electric spark, and observing the absorption  $m$ , the carbonic acid is absorbed by potassa. Let us always designate the hydrogen by  $x$ , the protocarburetted hydrogen by  $v$ , and by  $n$  the carbonic acid formed; we shall have,

$$\frac{3}{2}x + 2v = m,$$

$$v = n,$$

whence

$$x = \frac{2m - 4n}{3},$$

and

$$V = x + v;$$

which result may also be verified by determining the quantity  $a$  of oxygen consumed in the combustion, giving

$$\frac{x}{2} + 2v = a.$$

Hence is deduced the equation:

$$V + a = m + n,$$

which moreover exists for carburetted hydrogens, their mixtures with hydrogen, the mixtures of hydrogen with oxide of carbon, and, consequently, for all the mixtures of these various gases.

*Mixture of Oxide of Carbon and Protocarburetted Hydrogen.*

§ 1257. This mixture is exploded with a large excess of oxygen, in order to be able to measure exactly the last gaseous residue; there is again observed a decrease of volume  $m$ , and, by means of potassa, it is ascertained that a quantity  $n$  of carbonic acid has formed. If  $z$  and  $v$  still represent the proportions of oxide of carbon and hydrogen, we shall have

$$\frac{z}{2} + 2v = m,$$

$$z + v = n,$$

whence

$$z = \frac{4n - 2m}{3}, \quad v = \frac{2m - n}{3};$$

or, to verify it,

$$V = z + v.$$

By ascertaining the quantity of oxygen which has disappeared, there results

$$\frac{z}{2} + 2v = a;$$

whence is again deduced

$$V + a = m + n.$$

A certain quantity  $k$  of atmospheric air, and then an excess of oxygen, may also be added to the gas, taking care to avoid the condition in which nitrous products may be formed; but the first plan is preferable.

*Mixture of Nitrogen, Oxygen, and Protocarburetted Hydrogen.*

§ 1258. A quantity  $b$  of oxygen being added to the mixture in order that this gas may be in excess, the explosion is effected and the decrease of volume  $m$  marked; after which the volume  $n$  of carbonic acid, produced by absorption by potassa, is ascertained. Then is

$$2v = m,$$

$$v = n,$$

$$V = y + v + u.$$

The next step is to determine, by means of combustion with an excess of hydrogen, the quantity  $y'$  of oxygen which remains in the residue. If  $m'$  represents the decrease of volume effected by this combustion, we have

$$y' = \frac{m'}{3}.$$

We have, moreover, for the quantity of  $a$  of oxygen consumed in the first combustion,

$$2v = a,$$

consequently,

$$y = a + y' - b = a + \frac{m'}{3} - b,$$

whence may be deduced

$$\begin{aligned} v &= \frac{m}{2} = n, \\ y &= a + \frac{m'}{3} - b, \\ u &= V + b - a - \frac{m'}{3} - n. \end{aligned}$$

*Mixture of Nitrogen, Oxygen, Hydrogen, and Protocarburetted Hydrogen.*

§ 1259. This mixture frequently exists in air which has passed through the lungs; in which case the nitrogen predominates, and oxygen is present in much larger quantity than would be necessary to completely burn the combustible gases; but the mixture cannot be exploded. After adding gas from the battery, and observing the decrease of volume  $m$  which results, the quantity  $n$  of carbonic acid formed is ascertained, and these operations furnish

$$\begin{aligned} \frac{3x}{2} + 2v &= m, \\ v &= n; \end{aligned}$$

whence

$$x = \frac{2m - 4n}{3}.$$

The quantity  $y'$  of oxygen consumed by this combustion is

$$y' = \frac{x}{2} + 2v = \frac{m + 4n}{3}.$$

After these operations there remains a mixture of  $y''$  of oxygen and  $u$  of nitrogen, referred to the original volume, which is analyzed by the process explained in § 1246. The whole quantity  $y$  of oxygen contained in the mixture is

$$y = y' + y''.$$

As a measure of greater certainty, it is well to determine directly, by absorption, in another portion of the original gas, the whole quantity  $y$  of oxygen contained in the gaseous mixture, which thus affords a verification, proving the combustible mixture to be formed of hydrogen and protocarburetted hydrogen.

If the oxygen contained in the mixture were not sufficient to completely burn the hydrogen and protocarburetted hydrogen, a certain quantity  $a$  of oxygen, to be taken into account at the close of the experiment, would be added, and to this new mixture the process just described would be applied.

*Mixture of Nitrogen, Oxygen, Oxide of Carbon, Hydrogen, and Protocarburetted Hydrogen.*

§ 1260. We shall again suppose that the oxygen is present in sufficient quantity to completely burn all the combustible gases; for, if it were otherwise, a sufficient quantity of oxygen must be added, and the new mixture then be considered as the original gas.

The mixture is exploded in the eudiometer, either alone or after the addition of the gas from the battery; and the absorption  $m$  being marked, and the quantity  $n$  of carbonic acid produced determined, there results,

$$\begin{aligned} \text{I.} \quad & \frac{z}{2} + \frac{3x}{2} + 2v = m, \\ \text{II.} \quad & z + v = n, \\ \text{III.} \quad & y' = \frac{z}{2} + \frac{x}{2} + 2v. \end{aligned}$$

The gas which remains after these operations is composed only of nitrogen and oxygen, of which the quantities  $u$  and  $y''$ , which may from this time be considered as fixed, are next ascertained.

Lastly, in a fresh quantity of the original gaseous mixture, the whole quantity  $y$  of oxygen which exists in it is determined by absorption, which gives

$$\text{IV. } y' = y - y''.$$

The equations I. II. III., which are then sufficient for the calculation of the three unknown quantities  $x$ ,  $y$ , and  $v$ , give

$$x = m - y', \quad v = y' - \frac{m+n}{3}, \quad z = \frac{m+4n}{3} - y'.$$

*Mixture of Oxygen and Bicarburetted Hydrogen.*

§ 1261. If this mixture does not contain a sufficient quantity of oxygen, it is to be added in such a proportion, that after the explosion and absorption of the carbonic acid by potassa, there shall remain a residue of oxygen which can be exactly measured. It is, moreover, necessary that there should exist in the mixture a considerable proportion of inert gas, as, otherwise, the eudiometric tube might be broken by the violence of the explosion. If the proportion of bicarburetted hydrogen is very great, it is preferable to first measure in the apparatus a certain quantity of atmospheric air, and then introduce the gas to be analyzed, and, if it be necessary, a certain quantity of oxygen, but not enough to completely burn the combustible gas. After having effected the explosion, which is much less vivid than if the combustion were complete, an excess of oxygen is introduced and exactly measured, after which the mixture is again exploded in order to perfect the combustion; and, if the latter be feeble, it would be prudent again to pass the electric spark, after having added gas from the battery. Let  $m$  be the volume which has disappeared in the successive combustions, and  $n$  the volume of carbonic acid absorbed by the potassa; then, as 1 volume of bicarburetted hydrogen consumes 3 vols. of oxygen and produces 2 vols. of carbonic acid, we have, designating by  $w$  the volume of bicarburetted hydrogen,

$$\begin{aligned} 2w &= m, \\ 2w &= n, \quad \text{whence } m = n. \end{aligned}$$

In the last mode of operating there is less danger of bursting the eudiometer, and the formation of nitrous products is also avoided; for it would only take place in the second combustion, which generally disengages but little heat.

*Mixture of Hydrogen and Bicarburetted Hydrogen.*

§ 1262. In order to analyze this mixture, when the bicarburetted hydrogen is in small quantity, it is sufficient to mix it with a large excess of oxygen, explode it, and ascertain the volume of gas which has disappeared, and that of the carbonic acid absorbed by the potassa. The only precaution necessary is to add enough oxygen to enable the last gaseous residue to be measured. There then results

$$\begin{aligned} \frac{3x}{2} + 2w &= m, \quad \text{whence } w = \frac{n}{2}, \\ 2w &= n, \quad x = \frac{2}{3}(m - n). \end{aligned}$$

If the bicarburetted hydrogen exist in large quantities, it is better to effect the combustion at two periods, and in atmospheric air. In this case, a certain quantity of atmospheric air is first measured, to which the gas to be analyzed, the volume of which is exactly determined, and then a quantity of oxygen, is added, so that, with the oxygen contained in the air, there shall not be enough of that gas to effect complete combustion. The electric spark being passed, an excess of oxygen is added, with a small quantity of gas from the battery, if this be deemed useful, and the mixture is exploded a second time. The analysis may be verified by determining the quantity of oxygen which remains in the eudiometer after the combustion; after which the whole quantity  $y$  of oxygen consumed is known, furnishing the equation:

$$y = \frac{x}{2} + 3w.$$

A verification is always useful, and becomes indispensable when it is not certain that the gaseous mixture is composed only of hydrogen and bicarburetted hydrogen.

*Mixture of Oxide of Carbon and Carburetted Hydrogen.*

§ 1263. This analysis is made like the preceding, and with similar precautions. The relations giving the proportion of the two gases are

$$\begin{aligned}\frac{z}{2} + 2w &= m, & \text{whence } x &= 2(n - m), \\ z + 2w &= n, & w &= m - \frac{n}{2}.\end{aligned}$$

If  $a$  represent the volume of oxygen consumed, the following relations again exist:

$$z + w = V, \quad \frac{z}{2} + 3w = a, \quad \text{whence } V + a = m + n.$$

*Mixture of Protocarburetted and Bicarburetted Hydrogen.*

§ 1264. The analysis will be conducted as in the preceding cases; and the following equations will be found:

$$\begin{aligned}2v + 2w &= m, & \text{whence } v &= 2(n - m), \\ v + 2w &= n, & w &= \frac{2m - n}{2};\end{aligned}$$

to which the other relations must be added, from which are deduced the verifications,

$$\begin{aligned}v + w &= V, \\ 2v + 3w &= a, \\ V + a &= m + n.\end{aligned}$$

which again give

*Mixture of Hydrogen, Protocarburetted and Bicarburetted Hydrogen.*

§ 1265. The analysis is conducted as in the preceding case; but it now becomes necessary to determine the volume  $a$  of oxygen consumed in the combustion, which furnishes

$$\begin{aligned}\frac{3x}{2} + 2v + 2w &= m, & \text{whence } x &= 2(m + 2n - 2a), \\ v + 2w &= n, & v &= 6a - 7n - 2m, \\ \frac{x}{2} + 2v + 3w &= a, & w &= m + 4n - 3a.\end{aligned}$$

There remains only one verification given by the relation

$$V = x + v + w,$$

but which is reduced to the equation

$$V + a = m + n.$$

*Mixture of Oxygen, Protocarburetted and Bicarburetted Hydrogen.*

§ 1266. The analysis is conducted as in the preceding cases; and the following equations result:

$$\begin{aligned}2v + 2w &= m, & \text{whence } v &= m - n, \\ v + 2w &= n, & w &= \frac{2n - m}{2}, \\ y + v + w &= V, & y &= V - \frac{m}{2}.\end{aligned}$$

A verification is obtained by determining the quantity  $a$  of oxygen added, which has been used in combustion; which will give the relation

$$2v + 3w = a + y.$$

leading to the equation

$$V + a = m + n.$$

*Mixture of Nitrogen, Protocarburetted and Bicarburetted Hydrogen.*

§ 1267. The analysis will be conducted as in the preceding cases; and we shall have the relations

$$\begin{array}{ll} 2v + 2w = m, & \text{whence } v = m - n, \\ v + 2w = n, & w = \frac{2n - m}{2}, \\ u + v + w = V, & u = V - \frac{m}{2}, \end{array}$$

with a verification given by the relation

$$2v + 3w = a;$$

which is again reduced to

$$V + a = m + n.$$

*Mixture of Nitrogen, Oxygen, Protocarburetted and Bicarburetted Hydrogen.*

§ 1268. The analysis is made in the same way, taking care to determine, at the close of the experiment, the portion  $a$  of oxygen added, which has disappeared in combustions; and the relations are as follows:

$$\begin{array}{ll} 2v + 2w = m, & \text{whence } v = m - n, \\ v + 2w = n, & w = \frac{2n - m}{2}, \\ 2v + 3w = y = a, & y = \frac{1}{2}m + n - a, \\ y + u + v + w = V, & u = V + a - m - n. \end{array}$$

Eudiometric analysis furnishes no verification; but the quantity  $y$  may be directly determined by absorption.

*Mixture of Oxygen, Hydrogen, Protocarburetted and Bicarburetted Hydrogen.*

§ 1269. The analysis is again conducted as in the preceding cases, and the relations are the following:

$$\begin{array}{ll} \text{I.} & \frac{3x}{2} + 2v + 2w = m, \\ \text{II.} & v + 2w = n, \\ \text{III.} & \frac{x}{2} + 2v + 3w - y = a, \\ \text{IV.} & x + y + v + w = V. \end{array}$$

These four equations are not sufficient to determine the four unknown quantities; and in fact it is easily seen that one of them is a consequence of the other three, on account of a peculiar relation introduced by the data of the problem. By adding together III. and IV. there results

$$\frac{3x}{2} + 3v + 4w = V + a,$$

which becomes, on account of II.,

$$\frac{3x}{2} + 2v + 2w = V + a - n;$$

giving rise, in consequence of the chemical composition of the mixed gases, to the equation:

$$V + a - n = m, \quad \text{or,} \quad V + a = m + n,$$

which includes the equation I. in the other three.

In order to solve the question, the quantity  $y$  of oxygen must be determined directly by absorption, after which we have for the determination of the three other unknown quantities,

$$\begin{array}{ll} \frac{3x}{2} + 2v + 2w = m, & \text{whence } x = 2(m + 2n - 2a - 2y), \\ v + 2w = n, & v = 6a + 6y - 7n - 2m, \\ \frac{x}{2} + 2v + 3w = a + y, & w = m + 4n - 3a - 3y. \end{array}$$

*Mixture of Oxygen, Oxide of Carbon, Protocarburetted and Bicarburetted Hydrogen.*

§ 1270. The analysis is conducted as in the preceding cases, and from it are deduced the relations,

$$\begin{aligned}\frac{z}{2} + 2v + 2w &= m, \\ z + v + 2w &= n, \\ \frac{z}{2} + 2v + 3w - y &= a, \\ z + y + v + w &= V;\end{aligned}$$

which four equations are not sufficient to determine the unknown quantities, because they are connected together by the condition

$$V + a = m + n.$$

The quantity  $y$  of oxygen must be determined directly by absorption, which furnishes the equations

$$\begin{aligned}w &= a + y - m, \\ z &= \frac{2}{3}(2n + m - 2a - 2y), \\ v &= \frac{1}{3}(4m - n - 2a - 2y).\end{aligned}$$

*Mixture of Oxygen, Nitrogen, Oxide of Carbon, Protocarburetted and Bicarburetted Hydrogen.*

§ 1271. The analytic operations having been conducted as in the preceding cases, and the oxygen  $y=b$  having been determined by absorption, and lastly, the whole quantity  $a'$  of oxygen consumed in combustion having been equally ascertained, the following relations are established:

$$\begin{aligned}\frac{z}{2} + 2v + 2w &= m, \quad \text{whence } y = b, \\ z + v + 2w &= n, \quad z = \frac{2}{3}(m + 2n - 2a'), \\ \frac{z}{2} + 2v + 3w &= a', \quad v = \frac{1}{3}(4m - n - 2a'), \\ v &= a' - m, \\ z + y + u + v + w &= V, \quad u = (V - b) + a' - (m + n).\end{aligned}$$

Eudiometric analysis furnishes no verification.

*Mixture of Oxygen, Hydrogen, Oxide of Carbon, Protocarburetted and Bicarburetted Hydrogen.*

§ 1272. The analysis having been made as in the preceding cases, the oxygen  $y=b$  having been determined by absorbent reagents, and lastly the whole quantity  $a'$  of oxygen consumed having been equally determined, we have the relations

$$\begin{aligned}\frac{3x}{2} + \frac{z}{2} + 2v + 2w &= m, \\ z + v + 2w &= n, \\ \frac{x}{2} + \frac{z}{2} + 2v + 3w &= a', \\ x + z + v + w &= V - b;\end{aligned}$$

which four equations are not sufficient to determine the four unknown quantities  $x$ ,  $z$ ,  $v$ , and  $w$ , because the constant quantities are connected together by the relation

$$m + n = (V - b) + a',$$

which reduces the four equations to the four really distinct ones. A new relation between the unknown quantities must therefore be sought experimentally; and one can be obtained by determining exactly the specific gravity  $D$  of the mixture. By designating by  $d_x$ ,  $d_y$ ,  $d_z$ ,  $d_w$ , the respective densities of hydrogen, oxygen, oxide of carbon, protocarburetted and bicarburetted hydrogen, there results the relation

$$D = x d_x + y d_y + z d_z + v d_v + w d_w;$$



which new equation, added to the first four, renders the problem *algebraically* determinate.

A given quantity of the gaseous mixture may also be burned with oxide of copper, and the water formed weighed by using the apparatus described in § 1214. If  $p$  be the weight of the water obtained,  $W$  the volume of gas formed by the oxide of copper,  $t$  and  $H$  its temperature and pressure at the moment of being weighed; then will the weight of the gas burned be

$$W \cdot 0.001293 \cdot D \cdot \frac{1}{1.000367 \cdot t} \cdot \frac{H}{760},$$

and the ratio of the weight of water formed to the weight of gas burned will be

$$\frac{p}{W \cdot 0.001293 \cdot D \cdot \frac{1}{1+0.00367 \cdot t} \cdot \frac{H}{760}}.$$

On the other hand, let  $U$  be the constant volume to which the gas has been reduced by eudiometric analysis,  $\theta$  the equally constant temperature of the water in the cylinder, the elastic force of the original gas being  $V$ , we have, for the weight of the gas,

$$U \cdot 0.001293 \cdot D \cdot \frac{1}{1+0.00367 \cdot \theta} \cdot \frac{V}{760}.$$

If  $\pi$  designate the weight of water yielded by the gas when completely burned we should have, for the ratio between this weight and that of the gas,

$$\frac{\pi}{U \cdot 0.001293 \cdot D \cdot \frac{1}{1+0.00367 \cdot \theta} \cdot \frac{V}{760}},$$

whence the equation,

$$\frac{p}{W \cdot 0.001293 \cdot D \cdot \frac{1}{1+0.00367 \cdot t} \cdot \frac{H}{760}} = \frac{\pi}{U \cdot 0.001293 \cdot D \cdot \frac{1}{1+0.00367 \cdot \theta} \cdot \frac{V}{760}},$$

or simply,

$$\frac{p}{W \cdot \frac{1}{1+0.00367 \cdot t} \cdot H} = \frac{\pi}{U \cdot \frac{1}{1+0.00367 \cdot \theta} \cdot V};$$

whence

$$\pi = p \cdot \frac{U}{W} \cdot \frac{1+0.00367 \cdot t}{1+0.00367 \cdot \theta} \cdot \frac{V}{H}.$$

Now the weight of the water is equally expressed by

$$U \cdot 0.001293 \cdot 0.622 \cdot \frac{1}{1+0.00367 \cdot \theta} \cdot \frac{\frac{3x}{2} + v + w}{760},$$

giving rise to

$$\frac{3x}{2} + v + w = \frac{\pi \cdot 760 (1+0.00367 \cdot \theta)}{U \cdot 0.001293 \cdot 0.622};$$

which new relation may be introduced into the calculation.

*Mixture of Oxygen, Nitrogen, Hydrogen, Oxide of Carbon, Proto and Bicarburetted Hydrogen.*

§ 1273. This is the most complex mixture which will fall under our notice. Its eudiometric analysis will be conducted as in the preceding cases: after having determined directly the quantity  $y=b$  of oxygen by absorption, and burned a certain quantity of gas by oxide of copper to ascertain its weight of water formed, the carbonic acid formed during this combustion may also be collected and determined, which furnishes no new relation, but only a verification of the

quantity of carbonic acid  $n$  found in the eudiometric analysis. The relations are the following:

$$\begin{aligned} y &= b, \\ \frac{3x}{2} + \frac{z}{2} + 2v + 2w &= m, \\ z + v + 2w &= n, \\ \frac{x}{2} + \frac{z}{2} + 2v + 3w &= a', \\ x + z + u + v + w &= V - b, \\ \frac{3x}{2} + v + w &= \frac{\pi \cdot 760(1 + 0.00367 \cdot \theta)}{U \cdot 0.001293 \cdot 0.622} = A, \end{aligned}$$

to which may be added, if the density  $D$  of the gaseous mixture has been determined, the relation

$$xd_x + yd_y + zd_z + ud_u + vd_v + wd_w = D.$$

The problem is thus *algebraically* determined. If each of the numerical determinations were made with *mathematical precision*, the values of the unknown quantities, reduced by calculation, would be *strictly correct*. But, however carefully the operation may be conducted, each of these determinations is liable to slight error. Now, it is easy to be certain that by varying, by a very small quantity, each of the experimental data,  $b$ ,  $m$ ,  $n$ ,  $a'$ ,  $V$ ,  $A$ , and  $D$ , the value of the unknown quantities vary *often* by much larger quantities; and, by marking certain hypotheses, *properly selected*, on the composition of the gaseous mixture, it will be seen that by applying to the formulæ numerical data which differ very slightly, the calculated composition of the gaseous mixture ranges often between very extended limits. This observation is particularly applicable to the relation afforded by the density of the gaseous mixture, because the latter is composed of gases of which the individual densities, in general, differ but slightly. This relation must therefore be used with great caution.

We have supposed, in the preceding observations, that the nature of the elementary gases composing the mixture was known; but the question becomes much more difficult when this is not the case, and can, most frequently, only be answered by analysis, which must be most carefully conducted, and repeated several times; and the operator must satisfy himself that the relations which frequently exist between the experimental data, and which we have given in each case, are fulfilled. If the experimental data were mathematically exact, the formulæ suitable to the most complicated mixture might be applied to them at once, and the calculation would give no values for the gases which do not exist in the mixture. But, as these data are liable to trifling errors, small values for the gases which do not exist will generally be found, which values the operator must then examine with great care, and particularly the equations which often exist between the numerical data, in order to ascertain if these equations would not be rigorously fulfilled by the experimental data, by altering the latter by quantities equal to the extent of error to which each one is liable. None of the methods of analysis by absorption indicated (§1244) should be neglected while examining the errors which each may have produced on the gaseous residue, by the solvent action which the reagents exert on the gas composing this residue. Lastly, if the analyst is provided with large quantities of gas, he may, by subjecting them to suitably selected chemical reactions, obtain some light on the nature of the component gases.\*

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\* The method for analyzing complicated gaseous mixtures is due to Bunsen, who first employed them in his masterly investigation of the gases issuing from blast furnaces.—*W. L. F.*

## ESSENTIAL IMMEDIATE PRINCIPLES OF PLANTS.

§ 1274. A microscopic examination of the various component parts of plants shows them all to be constituted of cellular tissue, varying in form according to the part of the vegetable subjected to inspection. The cavities of the tissue are filled with very diversified matter; sometimes, as in the case of wood, the parietes of the cells are covered by a hard and brittle substance, called *lignine*, or *woody fibre*, which frequently almost completely fills their interstices; while at other times, as in the grains of the cerealia, potatoes, and other tubers, the cells contain a quantity of small ovoidal globules, varying in size, constituting *fecula*, or *starch*; and lastly, in the case of the young organs of plants, the cells contain only a more or less viscous fluid, holding in solution mineral salts and various organic substances, the principal of which are gums, gelatinous substances, and certain nitrogenous combinations, designated by the general name of *albuminous substances*. Oils or fat substances are frequently found in the cells, as in the oleaginous grains, sometimes in large quantities.

We shall begin by the study of these various substances, which are found in all members of the vegetable world, and which are essential to the existence of plants.

CELLULAR TISSUE, OR CELLULOSE,  $C_{12}H_{10}O_{10}$ .

§ 1275. The cellular tissue is particularly evident in the young organs of vegetables. The cell is formed in the liquids which circulate through the plant, and grows by successive agglutination with the cells previously formed, which occasions a modification in the original forms of the cells. Sometimes they are rounded, and show a certain regularity, as in the pith of the elder, (fig. 649,) and in the potato, in which case they constitute the *cellular tissue properly so called*. At other times the cells form elongated tubuli, communicating by their contracted extremities, as seen in fig. 650, which represents the

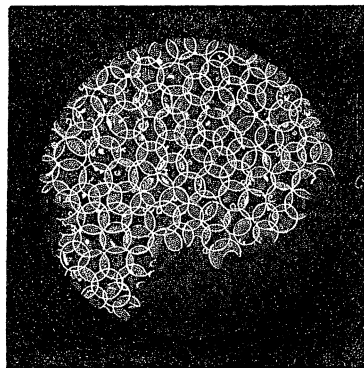


Fig. 649.

longitudinal section of a stalk of asparagus, of which a transverse section is seen in fig. 651; and in figs. 652 and 653, which exhibit

(fig. 653) a fibre of flax or hemp, and (fig. 652) a fibre of cotton : the tissue is then called a *vascular tissue*.

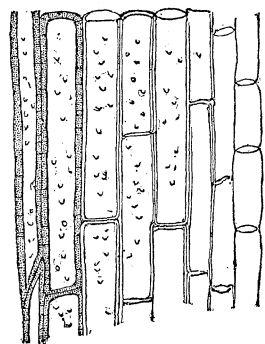


Fig. 650.

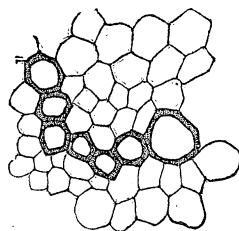


Fig. 651.

As the vegetable portions grow old on the living plant, the vascular vessels are filled with woody fibre, which increases gradually in thickness, and leaves only very narrow canals for the circulation of the sap.

The whole of this mechanism constitutes *wood*.

Among all the substances entering into the composition of plants, the cellular tissue is distinguished by its

great resistance to chemical agents—a resistance which allows its separation in a state of purity sufficiently perfect to permit the

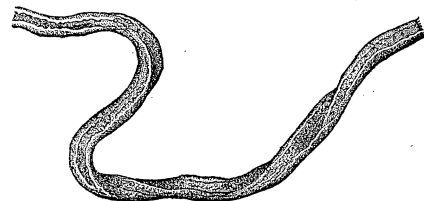


Fig. 652.



Fig. 653.

study of its chemical properties, and to ascertain its elementary composition. It has thus been found to be identical, *in this respect*, not only in all parts of the same plant, but also in all different vegetables. Chemists have given the name of *cellulose* to that

constant substance which they regard as forming the cellular tissue of all plants.

Cellulose is nearly pure in cotton, in which case it consists of the down of the cottonseed ; and in hemp and flax, that is in the textile fibres extracted from the plants of these names. Cellulose is also nearly pure in paper and old linen, which are made of the substances just mentioned, and which, during their preparation and use, have been subjected to various chemical reactions, which have gradually effected the entire destruction of the more changeable foreign substances, mixed with the cellular tissue properly so called.

Cellulose is extracted from various parts of plants by subjecting them to successive chemical reactions which destroy the more alterable woody fibre, the preparation being longer and more difficult in proportion to the quantity of woody fibre. The substance, when obtained in as disaggregated a form as possible, is digested with hot solutions of caustic potassa or soda, and, after washing the residue, is treated with weak chlorohydric acid, and washed with

water. By a repetition of this process for a certain number of times, the woody fibre may be completely removed; although the same result may be obtained more quickly by subjecting the substance to more powerful oxidizing reagents, such as a weak solution of chlorine or hypochlorite of lime, and following each of these treatments with an alkaline solution and dilute chlorohydric acid. Although these various reagents attack the cellular tissue itself, the action on it is much less active than on the substances surrounding it; so that if the operation be carefully conducted, and reagents diluted with water be alone used, the greater portion of the cellulose escapes destruction. It is washed successively with alcohol and ether to dissolve the fatty matter.

Pure cellulose, which is white and transparent, is insoluble in water, alcohol, ether, and the fixed or volatile oils. Dilute acid solutions have but little effect upon it, even at the boiling point, which is also true of sufficiently diluted alkaline solutions. The resistance which cellulose presents to these reagents varies with its cohesion; recently formed cellulose being much more easily changed than that of older date. Concentrated sulphuric and phosphoric acid attack cellulose, and cause it to undergo a remarkable metamorphosis: after converting it into a soluble substance, called *dextrine*, they change it to a sugary substance, or *glucose*. Fuming nitric acid combines, when cold, with cellulose, and converts it into an insoluble substance, eminently combustible and explosive, and which will be described hereafter. At the boiling point, nitric acid dissolves it, and oxalic acid is formed. Acetic acid, even in a concentrated state, has no action on cellulose.

Cellulose, as it exists in the untouched cellular tissue of plants, is not coloured by an aqueous solution of iodine; but when it has commenced to be disaggregated by sulphuric acid, it assumes a beautiful blue colour; which reaction is frequently used in the study of vegetables under the microscope, because it distinguishes the cellular tissue from certain nitrogenous membranes, which do not possess this property.

After some time, a solution of chlorine, or a hypochlorite, completely burns cellulose, forming water and carbonic acid; which combustion is rapid in a concentrated and hot solution of hypochlorite.

The elementary composition of cellulose is,

Carbon .....	44.44
Hydrogen.....	6.18
Oxygen.....	49.38
	<hr/> 100.00

The formula  $C_{12}H_{10}O_{10}$  is generally assigned to it; but as there are no means of determining its chemical equivalent, the formula representing its molecular composition may be a multiple of the

above. It will be remarked that hydrogen and oxygen exist in it in the proportions constituting water.

## LIGNIN.

§ 1276. It has been mentioned that the sides of the cells become generally incrustated with a substance formed at the expense of the organic substances dissolved in the sap; which constitution of ligneous matter is very well exhibited in fig. 654, representing a transverse section of a piece of oak-wood, as seen through the microscope. The black spaces are the canals which still remain in the cells; some of which former, as *a*, are larger, and appear to be principally used for the circulation of the sap. As the wood grows by annual concentric layers, easily counted in old trees, the centre layers are older than the external ones, and their cells are also much more incrustated with ligneous matter than the latter. The central layers of the trunk of a tree, constituting *the heart*, are therefore firmer and harder than the outer

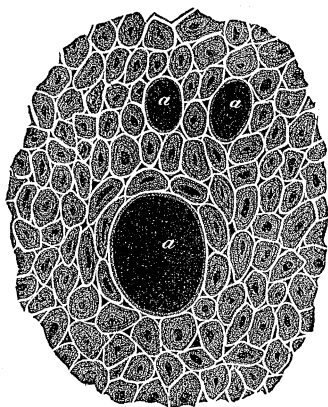


Fig. 654.

layers, forming the *sap-wood*; and they are also less subject to change, because they contain less sap and albuminous matter, which are the principal causes of the changes and rotting of wood.

Although pure ligneous matter is sometimes deposited in the cells, resinous substances, which colour the wood and increase its combustibility, are generally precipitated at the same time; while pellicles of nitrogenous matter are also formed.

No way of isolating the ligneous matter in a state of purity being known, it has hitherto remained undecided whether the chemical composition of this substance is always identical; but sensible differences, which are observable in chemical reactions on the ligneous matter of various parts of vegetables, may possibly be produced by greater or less aggregation of the substance. Sawdust, successively subjected to the action of water, alcohol, and ether, presents a mixture of cellulose, lignine, a small quantity of nitrogenous matter, and several insoluble mineral salts; and by analysis it is found to contain more carbon and hydrogen than pure cellulose: thus, lignine contains more carbon than cellulose, and hydrogen exists in it in a proportion larger than that which would form water with oxygen. The following tables exhibit the elementary composition of several kinds of wood, previously dried in vacuo at a temperature of 212°:

*Wood from the Trunk of the Tree.*

	Beech.	Oak.	Birch.	Aspen.	Willow.
Carbon.....	49.46.....	49.58.....	50.29.....	49.26.....	49.93
Hydrogen....	5.96.....	5.78.....	6.23.....	6.18.....	6.07
Oxygen.....	42.36.....	41.38.....	41.02.....	41.74.....	39.38
Nitrogen.....	1.22.....	1.23.....	1.43.....	0.96.....	0.95
Ashes.....	1.00.....	2.03.....	1.03.....	1.86.....	3.67
	100.00.....	100.00.....	100.00.....	100.00.....	100.00

*Wood from the Branches.*

	Beech.	Oak.	Birch.	Aspen.	Willow.
Carbon.....	50.37.....	50.08.....	51.29.....	49.59.....	51.39
Hydrogen....	6.21.....	6.14.....	6.17.....	6.20.....	6.18
Oxygen.....	41.14.....	41.38.....	40.41.....	40.23.....	36.45
Nitrogen.....	0.78.....	0.95.....	0.87.....	1.00.....	1.41
Ashes.....	1.50.....	1.45.....	1.26.....	2.98.....	4.57
	100.00.....	100.00.....	100.00.....	100.00.....	100.00

§ 1277. Wood is decomposed after some time, when subjected to the simultaneous influence of air and moisture, by the influence of a species of fermentation owing to the presence of nitrogenous albuminous substances, and carbonic acid is disengaged, while the wood is converted into a brown or black substance, called *humus*, or *mould*; an alteration which is the more rapid when the wood is of recent formation, because its canals, being less incrustated with woody fibre, contain more sap, and, consequently, more albuminous nitrous matter, which is the principal cause of the change. This substance, by its alteration, gives rise to true ferments, and serves as food for various insects which lodge in the wood and ultimately destroy it. If this be the cause of the rotting of wood, it might readily be prevented, if, by certain chemical agents, the alteration of the nitrogenous matter could be prevented, thus rendering it unfit for the food of animals. All poisonous substances which prevent the putrefaction of animal matter produce this effect; but the difficulty consists in making it penetrate all the vessels and cells of the wood. This question has attracted a good deal of attention in latter years, and several processes have been invented for its economical determination on a large scale.

The liquid containing the antiseptic substance has been made to penetrate the smallest vessels of the wood, by immersing one end of the trunk of a tree, of 2 to 4 metres in length, in a tub containing the solution, while to the other end is fitted a cast-iron vessel, in which a vacuum is produced by the combustion of tow soaked in alcohol. By repeating this operation 2 or 3 times, the liquid is forced by the pressure of the atmosphere to traverse the whole length of the trunk.

Advantage may also be taken of the vital circulation to cause the antiseptic fluid to penetrate trees when standing or when recently felled. When the tree is standing, it is sufficient to make at its foot two incisions, separated by an interval of a few centimetres, and wrap around it a bandage of water-tight stuff, which receives from a tub the liquid to be imbibed by the tree. The sap-wood, of which the canals are very open, is soon injected with the liquid, which, however, penetrates with more difficulty into the heart and the parts thickly incrustated with lignine. When the liquid is coloured, this irregular impregnation is manifested by the differences of shade and by veins, which often gives to the boards an appearance rendered very beautiful by polishing.

Lastly, a process called *displacement* is sometimes used successfully, which consists in placing the recently felled tree in a horizontal position and surrounding the trunk near its butt with a water-tight bag, held in place by a band over a pad of clay, and pouring into the bag the antiseptic liquid by means of a tube entering a tub placed somewhere near. The liquid displaces the sap and takes its place. In this way, the delicate woods, such as the pines and firs, may be rapidly and uniformly injected, but it is not so in the case of hard woods; as, although the sap-wood is soon injected, the liquid penetrates with difficulty and irregularity into the heart of the tree. This process has been greatly improved, for railroad sleepers, in the following manner:—A piece of wood, of twice the length of the sleeper, being sawed in the middle to within 3 or 4 centimetres of the opposite side, and the crack opened with a wedge, between the vertical sides of the crack a tarred rope is interposed, which, being strongly compressed when the wedge is removed, closes the sides hermetically and forms a small narrow reservoir in the middle of the piece of wood. The antiseptic liquid, being then poured into this reservoir, ultimately penetrates the whole piece of wood.

Of the many chemical substances which may be used for this purpose, the *pyrolignite of iron* or impure acetate of the protoxide of iron is generally preferred, on account of its efficiency and low price. This substance, which is obtained by means of the acid liquid produced by the distillation of wood in close vessels, contains, in addition to the acetate of iron, creasote and tar, which assist in the preservation of the wood.

Wood is frequently covered with tar and a substance called *marine glue*, made by melting together 1 part of gum shellac and 2 parts of essence of coal-tar.

#### NITROGENOUS OR ALBUMINOUS VEGETABLE SUBSTANCES.

§ 1278. The nitrogenous matter of plants, designated under the general name of *albuminoid substances*, play an important part in vegetable physiology; but as they have hitherto been but imper-



fectly studied, we shall only state what is with certainty known concerning them.

All these substances are solid; some being soluble in water, as albumen, vegetable casein, and legumin; while others are insoluble, as gluten. They are decomposed by heat, and exhale an odour similar to that peculiar to burnt feathers, giving rise to empyreumatic gases and products, and leaving as an ultimate residue a black and brilliant spongy coal, the separation of which has been preceded by the fusion and swelling of the original matter. These substances may be indefinitely preserved after being perfectly dried; and in the moist state they can be preserved for a long time, if protected from the air; while, when placed under the simultaneous influence of air and water, they soon decompose, rot, and call into existence a host of microscopic animalculæ.

All albuminous substances dissolve in caustic potassa and soda, and, on adding an acid to the solution, a nitrogenous substance separates, in the form of grayish flakes, which contract, on drying, into a hard and brittle mass, while at the same time a decided smell of sulphydric acid is disengaged, and the liquid contains a certain quantity of phosphoric acid. The name of *protein* has been given to this nitrogenous substance, which appears to form the essential principle of all albuminous matter. It is not yet known with certainty in what state the sulphur and phosphorus exist in these substances; but some chemists suppose albuminous substances to be compounds of protein with different proportions of *sulphimide*  $\text{NH}_2\text{S}$ , and *phosphimide*  $\text{NH}_2\text{Ph}$ . These sulphuretted and phosphuretted substances are moreover found in very minute quantities in them.

In order to separate protein from the alkaline liquid, acetic acid must be used, because the majority of the mineral acids combine with that substance. Protein is tasteless and inodorous; soluble in water, alcohol, ether, and the essential oils; soluble with alteration after some time in boiling water; and its composition is represented by the formula  $\text{C}_{36}\text{H}_{25}\text{N}_4\text{O}_{10}$ .

Protein combines with acids, forming compounds soluble in water, but which are precipitated by the addition of a great excess of acid, and which are decomposed by the alkalies with the precipitation of the protein, which is again dissolved if an excess of alkali be added. Chlorohydric acid yields with protein, and, in general, with all albuminous substances, a blue liquid. Weak sulphuric acid destroys protein at the temperature of  $212^\circ$ , forming several new products, among which is distinguished a white crystallizable substance, called *leucin*.

Nitric acid acts powerfully on protein, forming a yellow acid, called *xanthoproteic*, which combines, at the moment of its formation, with a portion of the nitric acid; but the compound is destroyed by boiling water and the xanthoproteic acid is precipitated. The

acid, which, when pure, is of an orange-yellow colour, pulverulent, and tasteless, combines with mineral bases and acids, yielding compounds of a more or less deep yellow colour. The xanthoproteates of potassa, soda, and ammonia are soluble; and the other salts, which are all insoluble, are easily obtained by double decomposition.

This reaction of nitric acid on protein is frequently applied in the study of vegetable anatomy to detect albuminous substances, since they are the only ones which turn yellow by contact with nitric acid. There is a still more delicate test in the reddish colour assumed by albuminous solutions when in contact with a mixture of nitrate and nitrite of mercury, which is easily obtained by dissolving mercury in an equal weight of nitric acid containing  $4\frac{1}{2}$  equivalents of water, and then diluting the liquid with twice its volume of water. This liquid reacts, when cold, on albuminoid substances, and the discoloration is more rapid when it is heated to  $212^{\circ}$ .

Chlorine attacks protein suspended in water, and converts it into a white flaky substance, regarded as a *chlorite of protein*, because its composition is represented by the formula  $C_{36}H_{25}N_4O_{10}ClO_3$ . This substance, treated with an alkaline solution, loses its chlorine, disengages ammonia, and is converted into a soluble substance, called *tritoxide of protein*, because its composition corresponds to the formula  $C_{36}H_{25}N_4O_{12}HO$ . Chlorine produces a similar reaction on all albuminous matter; and the same substance is also formed when water containing albumen in suspension is boiled for several days.

Protein also combines with the alkaline earths, forming a pitchy substance, which becomes very hard by drying; which property is applied to the manufacture of a luting made of white of egg and slaked lime, (§ 661.)

### *Albumen.*

§ 1279. Albumen is a principle widely disseminated throughout plants, and existing in them either coagulated in their tissues or dissolved in the liquids which circulate through their vessels. It is also largely found in the animal economy: the serum of the blood and the white of the egg are essentially composed of a solution of albumen in water. Animal albumen appears to be identical in composition and chemical qualities with vegetable albumen, and many physiologists admit that this substance is furnished immediately to animals by the plants on which they feed.

Albumen assumes two very distinct forms: *soluble albumen*, and *coagulated* or *insoluble albumen*; and in both states, its chemical composition is the same. They will be easily understood by comparing the albumen of a raw egg to that of one when cooked. The albumen of an egg begins to coagulate at about  $140^{\circ}$ , while that of human serum remains unchanged until about  $158^{\circ}$ ; and as a general rule, albumen coagulates with greater difficulty in proportion to

the quantity of water in which it is dissolved. Coagulated albumen no longer dissolves in water, but merely swells in it; while the substance obtained by evaporation, at a low temperature, from an albuminous fluid, dissolves, on the contrary, in cold water, yielding a stringy liquid. Liquid albumen generally presents an alkaline reaction, and turns the plane of polarization of luminous rays toward the left; serum of the blood and all albuminous liquids exhibiting the same property.\*

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\* A large number of substances in the organic kingdom exhibit a physical peculiarity belonging to their molecular constitution, which appears to be a special effect of organization, as it has hitherto not been observed in any inorganic substance. It consists in the property possessed by their molecules of impressing modifications on polarized light, which are analogous, in many respects, to those it experiences when passing through non-symmetrical crystallized bodies, which faculty has been called the *rotatory power*, from the character of the effects which it produces. In this note we shall endeavour to explain its mode of manifestation and the method of measuring its principal peculiarities; and the idea we shall give it will suffice to attach it, from this time, as a specific character, to substances which possess it, as they will be described. We shall subsequently explain one of its practical applications in detail, and show how it may be applied to the exact determination, in a solution, of the proportion of matter in it which exerts the rotatory power. But, in order that these phenomena may be understood by persons who have not made a special study of optics, it is necessary to recapitulate a few of the chief laws of this science, on which the theory of these phenomena is based.

When a simple ray of light, emanating directly from a luminous source, falls, at an angle  $i$ , on the surface of a transparent medium, a greater or less portion of the ray is reflected; and, if the medium is perfectly transparent and its surface polished, the portion of light not reflected traverses the medium. The plane containing the incident ray is called the *plane of incidence*, and the reflecting surface at the point of incidence is called the normal. The reflected ray remains in the plane of incidence, and its direction makes an angle  $i$  with the normal, equal to that which the incident ray makes with the same normal. The laws which the transmitted ray obeys, when the medium traversed is homogeneous in all directions, are the following:—If the transmitted ray is simple, it remains in the plane of incidence, and makes, with the normal, an angle  $r$ , so that there always exists between the angle of incidence  $i$  and that of refraction  $r$  the relation  $\frac{\sin i}{\sin r} = m$ ,  $m$  being a constant quantity for the same medium, and called the *index of refraction* of the medium.

The same laws apply to the case in which the ray of light, instead of falling from empty space on the medium, reaches it after having traversed a first medium equally homogeneous; and the constant quantity  $m$  is then the *relative index of refraction* of the two media, and equal to the ratio of the indices of refraction of these media with regard to the space.

The light of the sun is composed of an infinity of variously coloured rays, each of which has its own index of refraction; and if therefore a mass of solar light be passed through a transparent prism, the rays separate and yield a coloured image, the *solar spectrum*, elongated in the direction of the refraction; the rays which have the greatest index of refraction being the farthest removed from the direction of the incident ray. The light of burning bodies affords a similar spectrum, which differs from the solar spectrum in the ratio of intensity of the various coloured parts.

The portion of light reflected at the surface of separation of two media varies with the angle of incidence, and is smallest when this angle is 0, that is, when the incident ray is normal to the surface; while it increases with the value of this angle, and is equal to the incident light, when the angle of incidence is equal to 90°, in which case the light is wholly reflected. However, when the ray passes

Many chemical reagents coagulate albumen when cold. Alcohol reduces it immediately to the insoluble state; and ether produces the same effect, though more slowly.

from a first medium into a second, of which the index of refraction is more feeble, in which case the value of  $m$  is smaller than 1, the total reflection of the incident ray commences before the rasant ray; which occurs at all the incidences for which the relation  $\frac{\sin i}{\sin r} = m$  gives values for the  $\sin r$  greater than 1. Thus, the total reflection begins at the angle  $I$ , for which we have  $\sin I = m$ ; that is, the angle of total reflection.

By being reflected at the surface of separation of two media, the nature of light is remarkably modified; which is readily demonstrated by the apparatus, (fig. 655.)

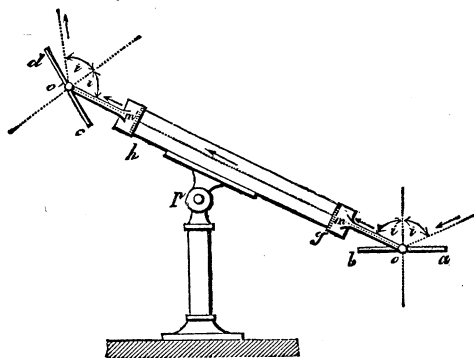


Fig. 655.

$ab$  and  $cd$  are two polished transparent mirrors which revolve around horizontal axes  $o, o'$ , perpendicular to the plane of the figure. The axes are supported by frames  $om, o'm'$ , mounted on drums  $ef, e'f'$ , which turn around the hollow cylinder  $gh$ , to which any inclination around the horizontal axis  $p$  can be given. A narrow bundle of rays is received on the first mirror  $ab$ , at an incidence  $i$ , and the whole instrument is arranged so that the reflected ray shall follow the direction of the axis of the cylinder  $gh$ . This reflected ray is received on

the second mirror  $cd$  at the same angle of incidence  $i$ ; and by turning the drum  $e'f'$  around the cylinder  $gh$ , all possible angles can be made on the second plane of reflection with the plane of reflection on the first mirror, without changing the angle of incidence  $i$ . Now, if the light reflected by the first mirror were still natural light, it would be always reflected in the same proportion on the second, whatever might be the azimuth of the plane of the second reflection compared with that of the first. But this is not the case, and the intensity of the light reflected by the second mirror diminishes in proportion as the azimuth of the second plane of reflection increases, and is a minimum when the azimuth is  $90^\circ$ ; its variations being moreover symmetrical around the azimuths  $0$  and  $90^\circ$ . By varying the common angle of incidence  $i$ , it can be ascertained that the variations of intensity of the light reflected on the second mirror in the various azimuths increase as we approach nearer the value of  $i$  given by the formula  $\tan i = m$ ,  $m$  being the index of refraction of the glass.

Light which possesses this property is said to be *polarized*, and the angle at which it must be reflected from a transparent medium to acquire it is called the *angle of polarization*: it will be seen that this angle depends on the index of refraction of the substance composing the mirror. Polarized light differs therefore from natural light in this, that while the latter is always reflected in the same proportion from a mirror inclined at the angle  $i$  with the incident ray, for all azimuths of the plane of reflection, polarized light is reflected in proportions varying with the azimuth of the plane of polarization; and, if the angle  $i$  satisfies the relation  $\tan i = m$ , there is a position of the plane of reflection in which the reflected ray is null. The plane perpendicular to this particular direction of the plane of reflection is called the *plane of polarization*.

When a ray of light falls on a mirror at the angle of polarization, the portion reflected is polarized in the plane of incidence; and if the properties of the refracted ray be examined by means of a second mirror which receives it at the

Albumen is extracted from flour by rubbing it with ten times its weight of cold water, allowing it to digest for several hours, decanting off the water, and digesting with an additional quantity of

angle of polarization, it is ascertained that the transmitted ray presents the properties of a ray partially polarized, or of a mixture of natural and polarized light; but the plane of polarization of the polarized portion is perpendicular to the plane of polarization of the reflected portion. It may therefore be admitted that when a ray of natural light falls on a mirror at the angle of polarization, a portion of the light traverses the mirror without modification, but that the other portion is divided into two bundles polarized in planes perpendicular to each other; and while the first bundle, which is polarized in the direction of the plane of incidence, is reflected, the second, polarized perpendicularly to this plane, is refracted. We recognise, moreover, that these two rectangularly polarized bundles are equal to each other, and that their union produces natural light; which may therefore be regarded as formed by the union of two equal bundles, polarized at right angles.

When the bundle of light which has traversed a first mirror at the angle of polarization traverses a second at the same angle, a portion of the natural light is divided into two bundles rectangularly polarized; and the bundle polarized in the direction of the plane of reflection is reflected, while the bundle polarized perpendicularly to this plane is refracted and joins the portion polarized by the first refraction. After its passage through the second mirror, the bundle contains a portion of polarized light much greater than when it left the first. Transmission through a third mirror again increases the polarized portion; so that after passing through a sufficient number of mirrors, at the angle of polarization, the bundle of natural light is entirely separated into light polarized in the direction of the plane of incidence which is reflected, and into light polarized perpendicularly to the plane of incidence which traverses the mirrors.

Crystallized media which do not belong to the regular system, effect immediately the separation of natural light into its two rectangularly polarized bundles. A bundle of natural light which falls on a rhomboid of Iceland spar, is divided in the crystal into two bundles, of equal intensity, polarized rectangularly, and which separate because they obey different laws of refraction. One of these bundles is polarized in the direction of the plane of the principal section of the rhombohedron; while the plane of polarization of the second is perpendicular to the plane of the principal section. The first obeys the ordinary laws of the refraction of light in homogeneous media, and remains in the plane of incidence, the law  $\frac{\sin i}{\sin r} = m$  being satisfied for all incidences; for which reason it is called the *ordinary ray*.

The second ray obeys very different laws: it remains in the plane of incidence only when this plane coincides or is perpendicular to the plane of the principal section, and it is only in this case that it satisfies a law  $\frac{\sin i'}{\sin r'} = m'$  similar to that which the ordinary ray obeys. In all other directions of the incident ray the law of the second refracted ray is more complex; on which account this ray has been called the *extraordinary ray*.

These two rays do not separate sufficiently to form two isolated images, except when the rhomb of spar is very thick; but a great separation may be produced by replacing the rhomb of spar by a prism cut out of this mineral; so that the edges of the prism shall be perpendicular to the principal section of the rhombohedron. When the refracting angle of the prism is only  $5^\circ$  or  $10^\circ$ , the two bundles separate sufficiently, but the images are coloured if the incident ray is not simple. This discoloration is avoided by gluing to the prism of spar a glass prism of a proper angle, the refraction of which, acting in a direction contrary to that of the prism of spar, almost entirely destroys the dispersion of colours. This apparatus, which is frequently used in the study of polarized light, is called an *achromatic birefracting prism*; and it enables us to examine, with ease, the properties of light polarized by reflection from a mirror: when used for this purpose, it is often called an *analyzing prism*. If the light is completely polarized in the direction of the plane of reflection, it is evident that when the plane of the principal section of the birefracting prism coincides with the plane of reflection, all

flour. After having repeated this operation three or four times, a liquid is obtained containing a certain quantity of albumen, which can be separated by evaporation at a low temperature.

the light will traverse the prism in the state of an ordinary ray, and the extraordinary ray will be extinguished. When, on the contrary, the plane of the principal section is perpendicular to the plane of polarization of the ray, the light will pass wholly in the extraordinary ray, and the ordinary ray will be null. In all the intermediate azimuths of the principal section of the birefracting prism, there will be an ordinary and an extraordinary image; and their relative intensities will vary according to the position of the principal section. The law of these variations is very simple: let  $\epsilon$  be the angle which the plane of the principal section of the birefracting prism makes with the plane of original polarization; and  $I$  the intensity of the polarized ray which falls on this prism: the intensity of the ordinary ray is  $I \cos^2 \epsilon$ , and that of the extraordinary ray  $I \sin^2 \epsilon$ : in all cases the rays are complements of each other, for we always have  $I \cos^2 \epsilon + I \sin^2 \epsilon = I$ .

The birefracting prism is very convenient for determining the direction of the plane of polarization of a polarized ray; as it is sufficient to find the direction to be given to the plane of the principal section of the prism, in order that the extraordinary fasciculus furnished by the normal incident ray may become null.

In order to understand the modifications experienced by polarized light when it traverses various media, the apparatus represented in fig. 656 is frequently used; in which  $ab$  represents a polished mirror, receiving the luminous rays at the angle of polarization, and reflecting them in the line  $cd$ , while at  $n$  is an achromatic bi-

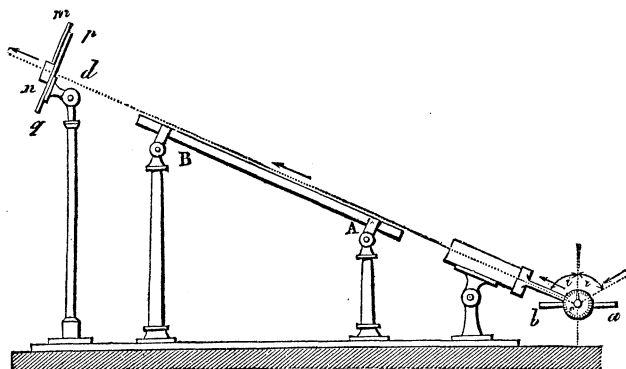


Fig. 656.

refracting prism, mounted on the centre of a movable index  $mn$ , which moves on a graduated circle  $pq$  perpendicular to the line  $cd$ . The plane of polarization of the ray reflected by the mirror being vertical, the extraordinary image afforded by the birefracting prism will vanish when its principal section is in the vertical plane, and the alidade will then correspond to 0 of the division.  $AB$  is a support on which various transparent media, which will be traversed by the polarized ray, as, for example, fluids contained in tubes, can be placed. Fig. 657 represents the longitudinal section of one of these tubes; which is composed of a tube of thick glass, generally enclosed in a metallic tube to which are fitted the two ferrules  $m, n$ , which support the glass plates closing the ends of the tubes.

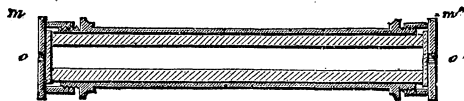


Fig. 657.

be placed on the support, so that the ray of polarized light may be obliged to tra-  
Vol. II.—20

In order to extract albumen from potatoes, they are cut into thin slices, which are digested in water containing two per cent. of sulphuric acid. The water is decanted after twenty-four hours, and

verse the liquid before reaching the birefracting prism, it will be seen that the ray has suffered no essential change in its properties by its passage through the fluid; it is still completely polarized, and its plane of polarization remains vertical. But, on substituting for pure water several other liquids, as, for example, a solution of cane-sugar, the properties of the polarized light are completely modified. Thus, before the interposition of the tube containing the solution of sugar, the extraordinary image of the birefracting prism is null when the index marks  $0^\circ$ ; and the image reappears if the tube be interposed. Nevertheless, the light has not been depolarized by its passage through the solution of sugar, and remains completely polarized; but its plane of polarization is no longer vertical, and it has been deviated by a certain angle toward the right of the observer who looks through the birefracting prism; and, in fact, if the index be turned to the right by a certain angle  $\alpha$ , the extraordinary image disappears entirely. The solution of sugar has, therefore, *turned toward the right, by an angle  $\alpha$ , the plane of polarization of the light*. If tubes of different lengths be filled with the same solution of sugar, it will be found that *the angles of deviation are in proportion to the lengths of the tubes*. On filling a tube of uniform length, successively, with solutions more and more rich in sugar, it is found that *the angles of deviation  $\alpha$  are in proportion to the quantities of sugar contained in the same volume of liquid*. It may, therefore, be said in general terms that *the deviations, or rotations, of the plane of polarization are in proportion to the number of molecules of sugar which the luminous ray meets in its passage*. Let  $\alpha$  be the deviation impressed by a homogeneous liquid on the plane of polarization of the simple ray, acting on it under the same circumstances, through units of space and with an imaginary density equal to unity. The density becoming  $\delta$ , without any change in the energy of the molecular action, the deviation, through the unity of thickness, will be  $[\alpha] \delta$ : then, the length becoming  $l$  for the same density, the total deviation will be  $[\alpha] l \delta$ . If, therefore,  $\alpha$  represent the deviation observed experimentally, we shall have

$$[\alpha] l \delta = \alpha, \text{ whence } [\alpha] = \frac{\alpha}{l \delta}.$$

The quantity  $[\alpha]$  is characteristic of the active substance; and is the same, at equal temperatures, for all the values of  $l$  and  $\delta$ , and may be considered as the *molecular or specific rotatory power* of the homogeneous liquid observed.

We have supposed that the polarized ray was simple light; which condition, though strictly fulfilled with difficulty, can nevertheless be sufficiently satisfied by placing between the birefracting prism and the eye a glass coloured red by sub-oxide of copper, which allows the red rays only to pass, and extinguishes all the others.

When the polarized ray is composed of white light, and traverses a medium endowed with a moderately powerful rotatory power, the extraordinary ray is not extinguished in any position of the birefracting prism; and the two bundles display very beautiful colours, which are always *complementary* in the two images: that is to say, which are such that they reproduce white light when superimposed on each other. It is easy to calculate these discolorations *a priori*, when the deviations  $\alpha_1, \alpha_2, \alpha_3$  are known which the medium exerts on the plane of polarization of each simple ray, and the intensities  $i_1, i_2, i_3$  of these rays in white light. Let us suppose, in fact, that the plane of the principal section makes an angle  $\epsilon$  with the vertical plane of the primitive polarization of all the rays. This plane will make an angle  $\alpha_1 - \epsilon$  with the plane of polarization deviated from the first ray, and, if the medium possessing the rotatory power is *colourless*, that is, if it allows the simple rays to pass precisely in the proportion in which these rays exist in white light, the intensity of the first ray in the ordinary image will be  $i_1 \cos^2(\alpha_1 - \epsilon)$ , and the intensity of the same ray in the extraordinary image will be  $i_1 \sin^2(\alpha_1 - \epsilon)$ ; so again the second ray will give in the ordinary image  $i_2 \cos^2(\alpha_2 - \epsilon)$ , and in the extraordinary image  $i_2 \sin^2(\alpha_2 - \epsilon)$ ; while the third ray will give in the

allowed to rest for the same space of time on fresh slices of potatoes; when, after several similar operations, a yellowish liquid is obtained, which must then be saturated with a small quantity of potassa, taking care to preserve a slight acid reaction. The liquids, evaporated at a low temperature, yield soluble albumen, mixed with salts, and probably with dextrin; but if the liquid be boiled, the

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ordinary image  $i_o \cos^2(\alpha_s - \epsilon)$ , and in the extraordinary image  $i_s \sin^2(\alpha_s - \epsilon)$ , and so on.

The ordinary image will therefore be formed by the superposition of a portion  $i_o \cos^2(\alpha_1 - \epsilon)$  of the colour of the first ray, a portion  $i_o \cos^2(\alpha_2 - \epsilon)$  of the colour of the second ray, a portion  $i_o \cos^2(\alpha_3 - \epsilon)$  of the colour of the third ray, and so on. The colour resulting from the ordinary image, and its intensity, may be calculated, by means of these elements, by a peculiar law established by Newton.

The colour and intensity of the extraordinary image will be calculated in the same way, by means of the constituent parts  $i_s \sin^2(\alpha_1 - \epsilon)$ ,  $i_s \sin^2(\alpha_2 - \epsilon)$ ,  $i_s \sin^2(\alpha_3 - \epsilon)$  of each of the simple rays which compose it.

Now, it has been observed, that for all media endowed with rotatory power, *with the exception of tartaric acid*, the relative deviations of the simple rays which constitute white light obey very nearly the same law: in other words, the deviations of the planes of polarization of the various simple rays are always proportional to each other. So that, instead of measuring the deviations produced by media endowed with rotatory power upon one simple ray, the red ray, for example, the deviations may be measured for which the ordinary and extraordinary image present identical hues. But all these hues cannot be measured with equal precision, because they are not all subject to variations equally sensible to the eye, for they have very small variations of the azimuth  $\epsilon$  of the principal section of the analyzing prism. The variations of tint are most sensible in a certain violaceous hue of the extraordinary image; because, however slightly the index may be turned to the right or left, the image passes suddenly from blue to red and from red to blue. This particular tint has been adopted by all experimenters, and is generally called the *tint of passage*, or *sensible tint*.

The white light of the sun, and particularly that transmitted through whitish clouds, can therefore be used; and in the comparison of the molecular rotatory powers of various active media, the formula

$$[\alpha] = \frac{\alpha}{l d}$$

can be applied, in which  $\alpha$  is the deviation of the index, in which the tint of passage has been observed. It is important, however, to remark that these measures will be exact only if the white light used in the observation is always composed of exactly the same materials, and this proposition is not rigorously accurate, at all times, as regards the light transmitted by the vault of heaven, in which blue light more or less predominates. It would be still more inaccurate to substitute for this the light of a lamp, the composition of which differs greatly from that of solar light. The result might also be very erroneous if the media were coloured; for, in that case, they would not allow the simple rays to pass in the proportions in which they exist in white light, and it then becomes necessary to make the observation with homogeneous light.

It is always useful, when the molecular rotatory powers of substances are to be measured by observing the tint of passage, to operate with tubes of suitable length, or with solutions so diluted that the angular deviations corresponding to the tint of passage shall differ but slightly; because the composition of the sensible tint differs remarkably in very diverse absolute deviations.

We have endeavoured, in the preceding note, to give a general idea of the special action which certain organic substances exert on polarized light. The reader who may desire to study this subject more deeply should consult the memoirs of M. Biot, to whom the discovery of these interesting phenomena, and their application to the study of a vast number of chemical phenomena, is due. (See *Annales de Chimie et de Physique*, 3e série, tomes x. et xi.)



albumen is precipitated, on the contrary, in flakes, and is then pure, but has become insoluble in water.

It is more easy to prepare albumen from animal liquids—for example, from serum of the blood or white of egg—as it is then sufficient to evaporate these liquids at a temperature below  $122^{\circ}$  to obtain it in the form of a transparent layer resembling paste. This substance, finely powdered, should be treated with ether, and then with alcohol, which dissolves the fatty substances, after which the residue is composed of soluble albumen mixed with salts. A purer albumen is obtained by pouring into the white of egg, or the serum, chlorohydric acid, which precipitates the albumen, by forming with it a scarcely soluble compound. The precipitate being separated and treated with a large quantity of water, which redissolves it, carbonate of ammonia, which precipitates the coagulated albumen in the form of white flakes, is poured into the liquid, and the precipitate, after being washed in water, dried, and then treated successively with water and alcohol, furnishes pure, but insoluble albumen.

The action of acids and alkalies on albumen is inferred from what has been said touching the action of the same substances on protein. We shall merely mention the difference of action exhibited by phosphoric acid in different degrees of hydration. Monohydric phosphoric acid  $\text{PO}_3\text{H}$  coagulates albumen immediately, while the trihydric acid  $\text{PO}_3\text{H}_3$  not only does not coagulate it, but will even dissolve the substance precipitated by the monohydric acid.

Albumen forms insoluble compounds with several metallic salts, particularly with corrosive sublimate, for which reason the white of eggs is used as an antidote in cases of poisoning by this medicine. On account of this property, also, corrosive sublimate is used in the preservation of anatomical specimens, as, by combining with the albumen, it prevents it from putrefying, and keeps worms from attacking them.

*Gluten, Vegetable Fibrine, Glutin, Vegetable Casëin.*

§ 1280. Gluten is most easily extracted from the cerealia, and principally from wheat, by making a thick paste with wheat flour, and kneading it under a stream of water until the water is no longer milky; when the water carries off the fecula and soluble matter, while a glutinous and elastic substance remains, which, when dried, is converted into a yellowish, translucent, and brittle mass, consisting chiefly of gluten, but containing likewise cellulose, some grains of fecula which have not been removed by the water, and fatty substances which can be dissolved in ether after the dried matter has been finely powdered. There are, in addition, substances which can be removed by treating them, when hot, first with concentrated, and subsequently with weak alcohol. The alcoholic liquors deposit, on cooling, a substance which resembles, in its composition and chemical properties, the casëin of cheese, for which reason it has re-

ceived the name of *vegetable casëin*. The alcoholic liquors, on cooling, deposit after evaporation a substance called *glutin*, having the same composition as albumen, and scarcely differing from it in its chemical properties.

To the substance left by gluten after these various processes, the name of *vegetable fibrin* has been given, which substance, in fact, presents the same composition as animal fibrin, which it closely resembles in its chemical properties. Vegetable fibrin combines with sulphuric acid, producing a compound soluble in pure water, and which dissolves in a weak solution of caustic potassa, furnishing a liquor resembling in its properties that produced by animal fibrin under the same circumstances.

*Legumin.*

§ 1281. Legumin is extracted from peas, beans, and lentils, which contain about 18 per cent. of it. They are chopped, and digested for two or three hours with tepid water, when the greater part of the legumin dissolves. In order to extract that which remains in the pulp, the latter is washed and again macerated with hot water, and the substance being expressed in a cloth and the liquid filtered, the legumin is precipitated from it by the addition of acetic acid. Some of the fatty substances are removed by treating the dried matter with ether and alcohol.

The substance thus obtained resembles starch, when it has been precipitated by acetic acid; and when dried, it forms a brilliant and transparent mass. Its aqueous solution is precipitated by alcohol and the acids; and it dissolves in the caustic alkalies, which appear to have no effect upon it. Its composition corresponds to the formula  $C_{90}H_{74}N_{15}O_{27}$ ; but the substance to which the name of legumin has been given is probably a mixture of several substances, which have not yet been separated.

AMYLACEOUS MATTER  $C_{12}H_{10}O_{10}$ .

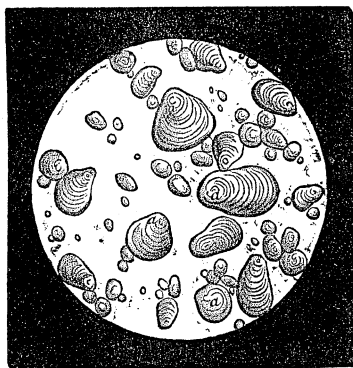


Fig. 658.

202

§ 1282. The name of *amylaceous matter* is given to a substance which forms rounded grains, varying in appearance, with which the cells of certain parts of plants are filled. That extracted from potatoes is commonly called *fecula*, and that obtained from the grains of the cerealia is known by the name of *starch*. When the fecula of the potato is examined by the microscope, it will be found to consist of ovoidal granules, the surface of each of which exhibits a particular point

*a*, the *hilum*, around which the substance is arranged in concentric layers.

On the surface of each granule curves can be perceived, which surround the hilum concentrically, and with apparent regularity. If



Fig. 659.



Fig. 660.

one of these grains be strongly compressed between two plates of glass, it breaks into several pieces, (fig. 659,) and all the planes of rupture generally pass through the hilum, as if the substance were less resistant at this point. Each grain is formed by the superposition of a great number of very thin pellicles, which sometimes ap-

pear immediately in the broken granules. They can always be shown by heating the fecula to  $392^{\circ}$ , a temperature which effects its disaggregation, and then moistening them with water, when the granules swell considerably, and the pellicles which compose them separate. Fig. 660 represents a grain of potato fecula which has begun to exfoliate. The pellicles may be rendered still more visible under the microscope, by moistening them with an aqueous solution of iodine, which turns them intensely blue. Two grains are frequently united together, and new pellicles of amylaceous matter are deposited on the united grains, thus forming a single irregular grain, having two hila.

By triturating a small quantity of fecula, for a long time, in a rough mortar, the greater part of the granules are burst, and if the broken grains be examined by the microscope, no appearance of liquid can be recognised, and

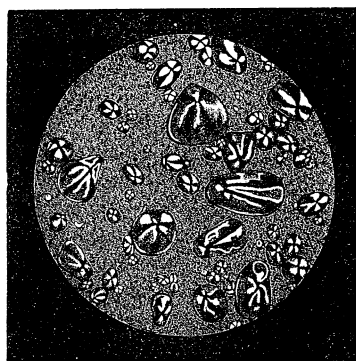


Fig. 661.

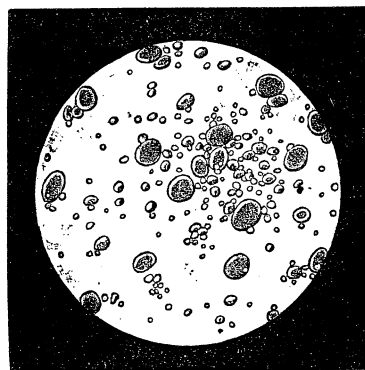


Fig. 662.

no portion of the substance can be dissolved in cold water. The entire grain is, therefore, formed of solid matter, and contains no gummy fluid, as was long supposed.

The hilum is not always as apparent in the amylaceous granules of other vegetables as in those of the potato, and can frequently only be shown by desiccation, which produces, at this point of the granules, a greater contraction than at the other points, and a depression which can be immediately recognised. The symmetrical arrangement of the amylaceous molecules around the hilum is particularly evident on examining by the microscope potato fecula illuminated by polarized light, (fig. 661,) and interposing a rhomb of Iceland spar between the object and the eye, when a black cross, of which the centre is lost in the hilum, is observed, analogous to that produced under the same circumstances by thin plates of crystal of the same axis, cut perpendicularly to this axis. Fig. 661 represents the same grains of fecula as fig. 658, but seen with polarized light.

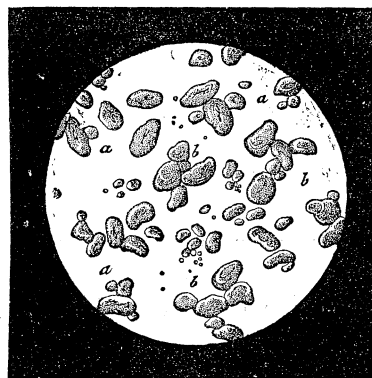


Fig. 663.

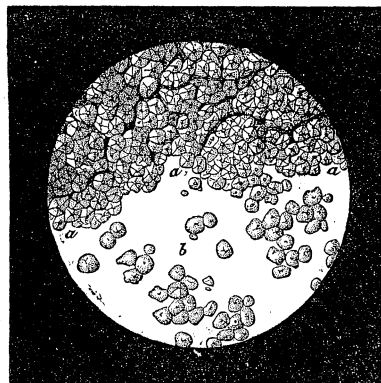


Fig. 664.

The amylaceous grains of several vegetables exhibit a peculiar appearance which enables an experienced eye to recognise immediately the vegetable to which they belong. This fact is easily proved by figs. 658, 662, 663, and 664, which represent amylaceous grains of various kinds, seen by the microscope and illuminated by natural light. In fig. 658 there are grains of potato fecula; in fig. 662, grains of wheat starch; in fig. 663 are seen the amylaceous grains of peas, (the grains *a* belonging to dried peas, and the grains *b* to green peas;) and lastly, fig. 664 represents the starch from Indian corn. Potato fecula is still more easily distinguished from other fecula when seen by polarized light, as it is the only one which exhibits in this case a well-marked black cross, (fig. 661.) By this character it is possible to discover by the microscope if wheat flour has been adulterated with potato starch.

The absolute size of amyla-

aceous grains varies greatly in different vegetables; and the following table gives the extreme length of the granules extracted from some of them:

Granules of potato.....	0.185 mm.
“ beans.....	0.075
“ sago.....	0.050
“ wheat.....	0.045
“ sweet-potato.....	0.040
“ Indian corn.....	0.025
“ millet.....	0.010
“ parsnip.....	0.007
“ mangel-wurzel.....	0.004

The grains of potato starch are collected in particular cells, nearly as is seen in fig. 665, which represents some full cells.

§ 1283. The amylaceous matter extracted from various vegetables presents exactly the same chemical composition, which is identical with cellulose, when the two substances have been dried under the same circumstances. Amylaceous matter, dried in vacuo at 284°, contains

Carbon.....	44.44
Hydrogen.....	6.18
Oxygen.....	49.38
	<hr/> 100.00

which composition corresponds to the formula  $C_{12}H_{10}O_{10}$ ; although it is generally admitted that 1 equivalent of oxygen and 1 equivalent of hydrogen exist in it in the state of water, notwithstanding that this water cannot be driven off without injuring the amylaceous matter. Chemists have therefore assigned to the substance supposed to be anhydrous the formula  $C_{12}H_9O_9$ , and the formula  $C_{12}H_{10}O_{10}$  to those dried in vacuo at 284°.

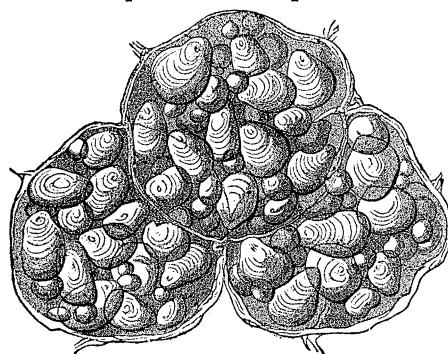


Fig. 665.

Amylaceous matter may exist in different states of hydration; and fecula, with only 1 equivalent of water, forms a very light powder, rapidly attracting the moisture of the air; but when exposed for some time to air which is far from its state of saturation, it increases 11 per cent., by absorbing 2 equivalents of water. The same state of hydration is obtained by drying the most hydrated fecula in vacuo, at the ordinary temperature. In moister air, it ab-

sorbs still 2 equivalents of water, and then contains 18 per cent. of it; and lastly, in air saturated with moisture it may still absorb 6 equivalents, so that it will contain in all 6 equivalents or 35 per cent. of water. In this state of hydration the grains adhere remarkably to each other, and the substance is easily compressed into balls. Moist fecula, recently extracted from the tubers, and merely separated from its water of combination by the absorbent action of plaster, retains 45 per cent. of water, and is called, in commerce, *green fecula*.

Fecula perfectly dried in vacuo, and then exposed to a temperature of  $536^{\circ}$ , assumes an amber colour without losing any of its weight; but not without being greatly modified, and transformed into a substance of the same chemical composition, but very soluble in water, and known by the name of *dextrin*. When the fecula has not been previously dried, this transformation is effected at a lower temperature, and it is still more rapid when heated in a tube hermetically sealed, preventing the evaporation of the water.

If water containing 1 or 2 hundredths of fecula be boiled, the latter swells and separates so as to appear to dissolve in the water; but if the liquid be then exposed to a temperature below  $32^{\circ}$ , it freezes, and the amylaceous matter becomes to a certain degree aggregated, and separates from the liquid in the form of small pelli-cles. When fecula is diluted with 12 or 15 times its weight of water, the temperature of which is slowly raised, all the grains ex-foliate on approaching the boiling point, and swell to such a degree as to occupy nearly the whole volume of the liquid, thus converting the latter into a gelatinous paste, which is used for pasting paper. The fecula swells also, even in cold water, if 1 or 2 hundredths of caustic potassa or soda be added to it.

Sulphuric, chlorohydric, phosphoric, and nitric acid also produce, when cold, the swelling and disaggregation of the amylaceous granules; the disaggregation being very rapid if the acid liquid contains at least 0.2 of real acid, while it follows in time, even when the quantity of acid is very small. When dilute acids are made to act on starch, at the temperature of  $212^{\circ}$ , the amylaceous matter is soon disaggregated, being converted first into *dextrin*, and then into a sugar-like substance, *glucose*, which both exert rotation toward the right. We shall again recur to this remarkable action.

When an aqueous solution of iodine is poured upon fecula, the latter turns of a beautiful blue colour; and the same discoloration is produced on starch in the state of paste, and even in the water in which it has been boiled. The colour changes with the more or less advanced stage of disaggregation of the fecula, and becomes insensible when the fecula has assumed the condition of dextrin soluble in water, even when cold. When water is heated containing fecula coloured by iodine, the blue colour disappears completely as soon as the temperature reaches  $150.8^{\circ}$ , and does not

reappear at a higher temperature; but on allowing it to cool, the colour reappears. These effects may be reproduced several times; but the intensity of colour lessens each time, because a portion of the iodine is vaporized.

Iodinated starch, suspended in water, is bleached by the action of solar light, the iodine being then converted into iodic and hydriodic acid. A few drops of chlorine will cause the colour to reappear, because they decompose the hydriodic acid, and set at liberty the iodine, which again seeks the starch. Alkaline solutions all bleach iodinated starch, by attacking the iodine, and the addition of an acid restores the colour.

Neither acetic acid nor ammonia act on fecula; while fuming nitric acid combines with amylaceous matter, and forms a compound insoluble in water, called *xyloidin*, which is regarded as a combination of 1 equivalent of amylaceous matter and 1 equivalent of nitric acid. If the nitric acid be hot, oxalic acid is immediately obtained.

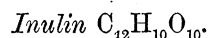
When fecula is ground with a concentrated solution of caustic potassa, it is converted into a substance which dissolves in cold water; and when a soluble salt of baryta or lime is poured into the solution, precipitates are obtained, which are compounds of the amylaceous matter with baryta or lime. By treating the precipitates with an acid, the amylaceous matter is again isolated, and the latter, in however separated a form it may exist, is again coloured blue by iodine.

Chlorine, in the presence of water, acts powerfully on fecula, and ultimately transforms it into carbonic acid and water. Concentrated solutions of the hypochlorites produce the same effect at a temperature of  $212^{\circ}$ .

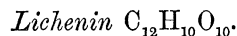
Cellulose, the chemical composition of which is the same as that of amylaceous matter, is not coloured blue by a solution of iodine; which reaction easily distinguishes the two substances in the microscopic study of the organs of vegetables. But when cellulose has been brought into contact for a few moments with sulphuric acid, it has acquired the property of turning blue by iodine; a fact which seems to prove that, by the influence of sulphuric acid, cellulose passes into a state in which it exhibits the properties of amylaceous matter.

§ 1284. In order to extract fecula from potatoes, the tubers are first reduced to a pulp, by means of a grater, which destroys their cells, and the pulp is then exposed to a current of water, which removes the fecula and conveys it into a proper receiver. The fecula is mixed with a small quantity of cellular tissue, which is easily removed by fresh levigation; for the grains of fecula, on account of their rounded form, fall to the bottom of the water, while the pellicles of cellulose, remaining longer in suspension, form the superficial layer of the deposit.

Wheat starch is made in the same manner, by working a paste of flour under a stream of water, as in the method of separating the gluten, (§ 1280;) when the water, after being allowed to rest, deposits the starch it held in suspension. If flour moistened with water be exposed to the air, it soon putrefies, but the nitrogenous matter alone is decomposed and changed into soluble products; so that, if the deposit be washed after some time, the starch, mixed with a small quantity of cellular tissue, only remains. The putrefaction of the gluten is hastened by pouring on the flour the water arising from a previous operation, which is called the *mother liquid* by manufacturers of starch.



§ 1285. Certain roots contain a peculiar substance, *inulin*, having the same composition as amylaceous matter, and appearing to play the same part, while its rotatory power is toward the left, contrary to that of amylaceous matter. Inulin is generally extracted from the root of the elecampane, (*inula helenium*;) for which purpose the bruised roots are digested with boiling water, and the solution clarified with white of egg; when the liquid deposits inulin on cooling, in the shape of a white powder. This substance, which is almost insoluble in cold, dissolves freely in boiling water; and if the water be boiled for a long time, the inulin is changed into a sugar-like substance. Inulin dissolves readily in acids, but, at the boiling point, it is more rapidly converted into sugar, without any change in the direction of the rotatory power. Boiling nitric acid converts it into oxalic acid, which transformation is probably effected only after intermediate stages of condition which have not yet been observed.



§ 1286. Several species of moss and lichen contain a substance, called *lichenin*, of the same composition as amylaceous matter, but differing from it in several points. It is generally obtained from Iceland moss, by digesting the chopped moss for 24 hours with 20 times its weight of cold water, to which a small quantity of carbonate of soda has been added, and repeating the washing until the water is altogether free from bitterness. The moss is then boiled with ten times its weight of water, and the boiling liquid expressed in a cloth; when, on cooling, it becomes a transparent jelly, which, after being dried, is a transparent, hard, and brittle mass, soluble in boiling water, from which alcohol precipitates it. If a solution of lichenin be boiled for a long time, it is no longer precipitated by cooling, and is converted into a gummy substance. Lichenin dissolves readily in acids, which convert it into sugar at the boiling point; and when heated with dilute nitric acid, it yields oxalic acid.

Gelatinous lichenin is coloured blue by iodine.



*Gums*  $C_{12}H_{10}O_{10}$ .

§ 1287. Certain substances, as yet imperfectly understood, which issue from trees, are called *gums*. Their elementary composition is the same as that of amylaceous matter, but they differ from it in several of their chemical properties: thus amylaceous matter forms oxalic with nitric acid, while, under the same circumstances, gums produce both oxalic and a peculiar acid called *mucic acid*.

Gums may be divided in three species:

1. Gum arabic, or *arabin*.
2. The gum of our indigenous fruit-trees, or *cerasin*.
3. Gum tragacanth, of which the essential principle has received the name of *bassorin*.

Gum arabic issues, in the form of a viscous solution, from certain species of acacia, and after some time the substance coagulates and dries on the tree. Large quantities of this gum are imported from Senegal.

Gum arabic is found in small round masses, having a conchoidal and vitreous fracture; and its taste is sweetish and nearly insipid. It dissolves, in indefinite proportions, in water, imparting to it a peculiar consistence, called *gummy*. It dissolves slowly in cold, and rapidly in boiling water; and the liquid, when evaporated, becomes more and more thick, and finally solidifies into a transparent mass, which presents no traces of crystallization.

The purest gum arabic of commerce has always a slightly yellowish tinge; but it may be made perfectly colourless by passing chlorine through a boiling solution of gum and drying the substance. Gum arabic, being insoluble in alcohol and ether, is precipitated from its aqueous solutions when alcohol is added; which method is sometimes adopted in proximate analysis to separate gum from sugars, which dissolve, on the contrary, very readily in dilute alcohol. The aqueous solution of gum arabic exerts a rotatory power toward the left.

Gum arabic, dried in vacuo at  $266^{\circ}$ , exhibits the same elementary composition as amylaceous matter dried under the same circumstances, and its formula is therefore  $C_{12}H_{10}O_{10}$ , or a multiple of it. Caustic potassa coagulates a concentrated solution of gum arabic; but if the solution is diluted, no precipitate is formed, although, by afterward adding alcohol, a compound of gum with potassa is formed. Subacetate of lead, poured into a solution of gum arabic, yields a white precipitate, of which the formula is  $PbO, C_{12}H_{10}O_{10}$ . Under these circumstances, therefore, gum arabic behaves like an acid.

Cold sulphuric acid, introduced into an aqueous solution of gum arabic, slowly inverts its primitive rotatory power, and changes it from the left to the right; the inversion ensuing more rapidly when assisted by heat; and if the liquor be boiled, the gum thus modified

is finally converted into a fermentable sugar, which also exerts a rotatory power in the latter direction. The transformation is effected by passing through a series of intermediate states, which may be observed, by saturating the acid with chalk, and precipitating by alcohol the already partially modified substance.

Cherry-trees, plum-trees, and various other fruit-trees exude a viscous matter, which solidifies in the air, and produces a gum called *cerasin*, probably a mixture of several substances. It swells in cold water, and dissolves with difficulty; but when boiled for a long time, a considerable portion of it dissolves, and the dissolved portion closely resembles arabin.

Gum tragacanth flows from certain vegetables of the genus *astragalus*, which are cultivated chiefly in the East: it exudes in the shape of a very thick gummy juice, which, on solidifying, forms small contorted strips. This gum is also probably a mixture of several substances; and the name of *bassorin* has been given to that which predominates and is regarded as its essential principle. Bassorin does not dissolve in water, even at the boiling point; but it swells and is converted into a gelatinous substance. It dissolves rapidly in the alkalies; while dilute sulphuric acid, at the boiling point, converts it into glucose.

Cerasin and bassorin, when treated with nitric acid, yield a mixture of oxalic and mucic acid; the formation of which latter, which is easily proved, because the acid is insoluble in cold water, is a very well-marked characteristic, by which gums may be distinguished from amylaceous matter.

Iodine does not colour gums when they are pure; and when gum tragacanth assumes a blue tinge, it is easily seen that this arises from the presence of a small quantity of fecula.

#### *Vegetable Mucilage.*

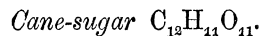
§ 1288. Many grains, such as flaxseed, and many leaves, stems, and roots of vegetables, as the mallow, marsh-mallow, borage, etc. etc., when macerated in cold, or better still, in boiling water, yield gummy and stringy liquids, in which alcohol produces a gelatinous precipitate, the nature of which has not been well ascertained. The general name of *vegetable mucilage* has been given to these substances. The mucilage of flaxseed presents, when dried, the same elementary composition as amylaceous matter and gums.

#### SUGARS.

§ 1289. *Sugars* are substances soluble in water, having a sweet taste, and possessing the property of being converted into alcohol and carbonic acid, when left in contact with certain nitrogenous organic substances, called *yeasts*, or *leaven*. Sugars are widely diffused through the vegetable kingdom; and three principal species have been distinguished by chemists.

1. Cane-sugar.
2. Grape-sugar.
3. The uncrystallizable sugar of fruits.

The first species is perfectly well known, while the others are less so; and when their properties are more accurately ascertained, they will probably be subdivided. A crystallizable substance, *sugar of milk*, is also found in the milk of animals, and should be classed among the sugars, from the definition we have just given of these substances; but we shall reserve its examination until the study of the fluids of the animal economy shall occupy our attention. In their composition, sugars present this remarkable fact, already remarked in other substances, that their hydrogen and oxygen exist in exactly the proportions which form water.



§ 1290. Cane sugar exists in solution in the juice of a large number of vegetables; and may be said to be found in all vegetables the juice of which is not acid, as acids react powerfully on cane-sugar, and convert it into fruit-sugar. Cane-sugar is also abundantly found in the sugar-cane, the sugar-beet, melons, turnips, carrots, the stalk of Indian corn, the ascending sap of the maple, the descending sap of the birch, and in a great number of tropical fruits, as the cocoa-nut, pineapple, etc. etc. It is principally derived from the sugar-cane and sugar-beet; and large quantities are also extracted from the sugar-maple.

Very pure cane-sugar is found in commerce, either in the form of large colourless and transparent crystals, constituting *sugar-candy*, or in that of small crystals adhering to each other, as in our common loaves of sugar. Cane-sugar is inodorous, possesses a very sweet taste, and its density is about 1.60. It dissolves in  $\frac{1}{3}$  of its weight of cold and in a still smaller quantity of boiling water; and the solution, when concentrated, produces, by evaporation at a low temperature, beautiful crystals. It dissolves in 80 times its weight of boiling absolute alcohol, but the greater portion of it is deposited during cooling; and it may be said to be nearly insoluble in cold alcohol. Sugar dissolves much more easily in slightly diluted alcohol, for 4 parts of alcohol at  $181.5^{\circ}$  will dissolve 1 of sugar. Cane-sugar melted or dissolved in water turns the plane of polarization of polarized light toward the right.

Cane-sugar fuses when heated above  $320^{\circ}$ , forming a viscous mass, flowing with difficulty, which solidifies into a transparent mass having a vitreous fracture. This mass, rolled out on marble tables, is sold under the name of *barley-sugar*; in making which article, confectioners are in the habit of adding a small quantity of vinegar before melting the sugar. In this state, the sugar is vitreous and transparent, but in a short time, especially if the air have access to it, the outer layers become opaque and fall in consequence

of the crystallization which takes place. Melted sugar, kept for some time at the temperature of  $356^{\circ}$ , loses the property of crystallizing when redissolved in water; and its constitution is, in that case, deeply altered.

The composition of crystallized cane-sugar and that of barley-sugar corresponds to the formula  $C_{12}H_{11}O_{11}$ .

If cane-sugar be heated to  $410^{\circ}$  or  $428^{\circ}$ , it loses 2 equiv. of water, and is converted into a black substance called *caramel*, of which the formula is consequently  $C_{12}H_9O_6$ . This substance is deliquescent, no longer tastes of sugar, is very soluble in water, which it turns of a deep brown colour, and acts the part of a weak acid, dissolving in the alkalies, and forming black precipitates with baryta and oxide of lead.

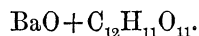
On continuing to heat caramel, it parts with more water, and is converted into a black insoluble product; and, lastly, if the temperature be still raised, acid products and inflammable gases are disengaged, while a puffy black coal remains. All these products are obtained mixed when sugar is suddenly heated.

When pounded or rubbed in the dark, sugar becomes phosphorescent; and when grated it has a slight taste of burnt sugar, owing to the production of a small quantity of caramel by the elevation of the local temperature.

When a solution of cane-sugar is boiled for a long time, the sugar undergoes alteration, which may be readily observed by examining the successive effects of the liquid on polarized light. It first loses the property of crystallizing, and closely resembles sugar which has been heated for some time to  $356^{\circ}$ ; which alteration is effectually prevented by the presence of a small quantity of alkali.

The mineral acids, even when very dilute, and the greater part of the organic acids, alter cane-sugar and transform it into a sugar which no longer crystallizes as formerly by evaporation, and which turns the plane of polarization of polarized rays toward the left. This new sugar may be called *sugar inverted by acids*, and in its chemical properties it closely resembles fruit-sugar. Acids which produce the same transformation undergo no change themselves, and are found intact in the liquor; and the transformation takes place with the mineral acids even when cold, and much more rapidly if the temperature be raised.

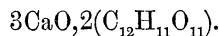
§ 1291. Cane-sugar combines with bases, and forms, in certain cases, crystallizable compounds, called *saccharates*. If concentrated water of baryta be poured into a concentrated boiling solution of sugar, a crystalline mass of saccharate of baryta is deposited on cooling, having for its formula



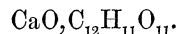
This salt bears a temperature of  $392^{\circ}$  without decomposing or

losing its water; but carbonic acid readily decomposes it, the sugar being redissolved and carbonate of baryta precipitated.

Two compounds of cane-sugar with lime may be obtained, the first of which is produced by pouring a solution of sugar upon an excess of slaked lime, when a compound, very soluble when cold, is formed, and can be separated by filtering. If the liquid be heated to boiling, the greater part of this compound is precipitated, since it presents the remarkable property of being much less soluble in hot than in cold water; so much so, that it may even be washed in hot and then redissolved in cold water. The formula of this saccharate, when dried at  $212^{\circ}$ , is

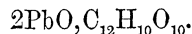


If, on the contrary, hydrate of lime be added, by small quantities at a time, to a concentrated solution of cane-sugar, until no more will dissolve, and then alcohol be poured into the liquor at  $185^{\circ}$ , a saccharate of lime is precipitated, of which the formula is

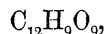


Solutions of saccharate of lime have a strong alkaline reaction; and they rapidly attract the carbonic acid of the air, causing the formation of small transparent crystals of carbonate of lime, resembling those of the native crystals of the substance, which are deposited on the sides of the vessel containing them.

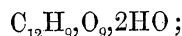
If finely divided protoxide of lead be digested with a concentrated solution of sugar in excess, an insoluble saccharate of lead is formed; and the liquid contains a small quantity of oxide of lead in solution. The same insoluble compound is obtained by pouring into a solution of sugar acetate of lead, which forms no precipitate, and then ammonia, which precipitates the saccharate of lead; when, by allowing the liquid and the precipitate to rest for some time in a hot place, they assume a crystalline appearance. The composition of saccharate of lead dried in vacuo corresponds to the formula



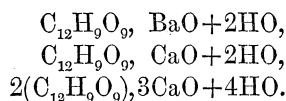
By being heated to  $320^{\circ}$ , it loses 1 equiv. of water, and its formula becomes  $2\text{PbO}, \text{C}_{12}\text{H}_9\text{O}_9$ ; and in both states of desiccation it yields, when decomposed by sulfhydric acid, a sugary liquor, which by evaporation produces sugar. The sugary substance has therefore undergone no permanent alteration by losing 2 equiv. of water, and it is reasonable to suppose then the formula of anhydrous cane-sugar to be



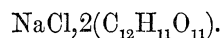
which would give for that of crystallized sugar



and the formulæ of the saccharates are



By evaporating a concentrated solution of 1 part of sea-salt and 4 parts of cane-sugar, crystals of sugar-candy are first formed, but the mother liquid subsequently deposits crystals having at the same time a sweet and a saline taste, of a deliquescent combination, of which the formula is



Chloride of potassium and chlorohydrate of ammonia form similar compounds, which often cause the loss of a large quantity of sugar, in the manufacture of beet-sugar, when the roots contain much sea-salt, as is the case when they have grown near the sea. As these compounds are deliquescent, they remain in the mother liquid or in the *molasses*.

The presence of sugar prevents the precipitation of several metallic oxides by alkalis, which is especially evident in the sesquioxides of iron and those of oxide of copper  $\text{CuO}$ , and which is readily explained, as the hydrates of the sesquioxide of iron and oxide of copper dissolve in a solution of sugar to which a certain quantity of potassa has been added.

Concentrated sulphuric acid blackens cane-sugar, and yields complicated products; its action when very dilute has already been described, (§ 1290.) Monohydrated nitric acid produces with sugar an insoluble, very combustible substance, analogous to that yielded by starch. The ordinary nitric acid of commerce attacks sugar when hot, and transforms it into a very soluble and deliquescent acid, to which the names of *oxalhydric* and *oxysaccharic acid* have been given. If the action of the nitric acid be much prolonged, a great deal of oxalic acid, which is finally converted into carbonic acid, is formed in the liquor.

At the boiling point sugar reduces several metallic salts; it precipitates suboxide of copper  $\text{Cu}_2\text{O}$  from the acetate of copper, and metallic copper from the sulphate and nitrate of this metal; and it precipitates metallic silver from the solution of nitrate of silver, at the same time disengaging products of the oxidation of sugar, such as formic, carbonic acid, etc. etc.

By distilling a mixture of 1 part of cane-sugar and 8 parts of quicklime, in a glass retort scarcely filled to one-half at a certain temperature, the mixture swells, gases are disengaged, and an oily liquid can be collected in a receiver properly cooled. The liquid, shaken with water, parts to it with a product  $\text{C}_3\text{H}_3\text{O}$  which is copiously obtained in the distillation of the acetates, and is known by the name of *acetone*. The liquid, exhausted by water, decomposes

nearly wholly, into an oily liquid  $C_6H_5O$ , boiling at  $183.2^\circ$ , and called *metacetone*.

*Sugar of Acid Fruits  $C_{12}H_{12}O_{12}$ .*

§ 1292. The second kind of sugar found in vegetables, and which is often called *uncrystallizable* or *fruit-sugar*, possesses the property of turning the plane of polarization to the left; and exists exclusively in the sour juices of vegetables, principally in fruits, as grapes, currants, cherries, plums, etc. etc. In order to extract it, the juice must be expressed, the acids saturated with chalk, the juice boiled with white of egg, which, by coagulating, removes the mucilaginous substances, and lastly, the liquid evaporated at a gentle heat. The substance thus obtained presents, when dried, the appearance of gum, being very deliquescent, dissolving largely in water, and even in alcohol at  $91.40^\circ$ , while it is insoluble in absolute alcohol. In contact with yeast it ferments immediately, and produces alcohol and carbonic acid. It is found already formed in the ascending sap of the birch and in the descending sap of the maple.

Cane-sugar is readily converted into this second species of sugar by boiling its solutions with dilute acids, which transformation also takes place, in the presence of these acids, when cold, as well as in that of organic acids, such as tartaric, citric, malic, and oxalic, but it requires a much longer time. Cane-sugar always undergoes this first transformation, under the influence of yeast, before that of fermentation properly so called, that is to say, before being converted into alcohol and carbonic acid. It is generally admitted that the uncrystallizable sugar of all fruits is identical, although this is by no means clearly proved, and several varieties will probably be found hereafter.

The chemical composition of sugar fuming to the left, dried in a water bath, corresponds to the formula  $C_{12}H_{12}O_{12}$ .

When a syrupy solution of this sugar is allowed to rest for some time, it deposits small crystalline grains of a sugary substance, which has been called, improperly, *grape-sugar*, being very different from the sugar which produced it, as its composition differs in containing, in addition, the elements of 2 equiv. of water, thus making its formula  $C_{12}H_{14}O_{14}$ . By dissolving it in water a liquor is obtained which is also very different from that afforded by the non-crystalline sugar which produced it: thus, while a solution of the latter turned the plane of polarization toward the left, a solution of the crystalline sugar turns it toward the right, like cane-sugar. This granular sugar differs, moreover, from cane-sugar, not only in its crystalline appearance, but also in the manner in which it behaves with various chemical agents, and by the intensity of its rotatory power. One of the most striking differences, and one of the most easy to prove, is, that cane-sugar, boiled with dilute acids, is converted into sugar

turning the plane of polarization toward the left; while under the same conditions, grape-sugar undergoes no change, and continues to turn toward the right.

*Grape-sugar*  $C_{12}H_{14}O_{34}$ .

§ 1293. We have just seen that the syrupy solution of sugar, turning to the right, yielded by sour fruits, as well as the liquor obtained by boiling cane-sugar with dilute acids, deposit, after a time, a sugary substance in crystalline grains, to which the name of grape-sugar has been given. It is the same substance which forms the white powder on dry grapes, or raisins, and which constitutes the grains of sugar found in the inside. If the pulp of these fruits, freed as much as possible from their crystalline granules, be treated with water, a solution is obtained which still contains a large quantity of sugar turning to the left.

The urine of patients labouring under a peculiar disease, called *diabetes mellitus*, or *saccharine diabetes*, contains sometimes 10 per cent. of a sugar, the chemical properties of which appear to be identical with those of grape-sugar. A precisely similar sugar is obtained when starch is boiled with a weak solution of sulphuric acid, and the solution is evaporated after having been saturated with chalk; which species is generally called *glucose*. The granular sugar found in honey appears to be identical with grape-sugar; and lastly, the same sugar is frequently separated from preserves made of acid fruits, in the form of crystalline crusts; in which case it has been produced by the alteration of the cane-sugar used in their manufacture, which, by virtue of the acids of the fruit, is converted into uncrystallizable sugar turning to the left, the latter product itself, in time, changing into grape-sugar.

Grape-sugar crystallizes with much more difficulty than cane-sugar, always producing a compound crystallization; and it is less soluble in water than cane-sugar, for it requires  $1\frac{1}{2}$  parts of cold water to dissolve 1 of grape-sugar. Its taste is also less sweet. Grape-sugar, on the contrary, dissolves somewhat more freely in alcohol than cane-sugar; as 1 part of it dissolves in 60 parts of boiling absolute alcohol, and in 5 or 6 parts of alcohol at 181.40. Solutions of grape-sugar turn the plane of polarization to the right.

The composition of crystallized grape-sugar corresponds to the formula  $C_{12}H_{14}O_{34}$ .

This sugar softens at about 140°, and is completely liquefied at 212°, at which temperature it loses 2 equiv. of water, and is converted into a new sugar of which the formula is  $C_{12}H_{12}O_{32}$ , and which then presents the composition of the fruit-sugar just described, although it continues to turn polarized light to the right. This latter sugar leaves, after evaporation, a pitch-like mass; but if this be allowed to rest for some time in contact with water, crystals of



grape-sugar are formed. If grape-sugar be further heated, it becomes brown and converted into caramel.

§ 1294. Grape-sugar combines less readily with bases than cane-sugar; and, when boiled with alkaline solutions, the liquor turns brown and exhales a smell of burnt sugar, acid products being formed which combine with the alkali. If slaked lime be poured into a solution of grape-sugar, a large quantity of the lime is dissolved, and the liquor first exerts an alkaline reaction, but at a later period becomes neutral, and carbonic acid no longer forms a precipitate. The sugar is then converted into a powerful acid called *glucic*, of which the formula is  $C_6H_5O_5$ , and which forms soluble salts with nearly all the bases; the formula of glucate of lime being  $CaO, 2C_6H_5O_5 + HO$ . The acid may be isolated by pouring oxalic acid into glucate of lime until no precipitate is thrown down; when, by evaporating the solution, a white acid is obtained, of a gummy appearance, very soluble in water and deliquescent. The acid forms with oxide of lead an insoluble salt of the formula  $2PbO, C_6H_5O_5$ , which is prepared by pouring subacetate of lead into a solution of glucate of lime. The glucate of lead, suspended in water, is readily decomposed by sulphhydric acid, and yields free glucic acid.

Glucic acid is also formed when a solution of cane or grape-sugar is boiled for a long time with sulphuric or hydrochloric acid.

When a solution of glucic acid is boiled in the air, the liquid turns brown, and a new acid, called *apoglucic*, is formed; and by saturating the liquor with chalk, after some time, acid glucates and apoglucates of lime are formed; after which the liquid is reduced to the consistence of syrup and treated with alcohol, which dissolves the acid glucate and leaves the apoglucate of lime. The latter salt, being redissolved in water, is treated with acetate of lead, which yields a precipitate of apoglucate of lead, which, while suspended in water, is decomposed by sulphhydric acid, and yields free apoglucic acid. Apoglucic acid is a brown, non-deliquescent substance, which readily dissolves in water, but very feebly in alcohol; and its formula, when dried at  $248^\circ$ , is  $C_{18}H_{11}O_{10}$ , while that of apoglucate of lead is  $PbO, C_{18}H_9O_8$ . The same acid is formed when solutions of the alkaline glucates are boiled in the air.

By pouring  $1\frac{1}{2}$  part of concentrated sulphuric acid gradually, and by small quantities at a time, upon 1 part of grape-sugar melted at  $212^\circ$ , treating it with water, and lastly saturating the liquor with carbonate of baryta, a large proportion of the baryta remains in the state of insoluble sulphate of baryta, while the liquid contains a soluble salt of baryta, the *sulphosaccharate*. If subacetate of baryta be poured into this liquid, a precipitate of sulphosaccharate of lead is formed, of which the formula, when it has been dried at  $338^\circ$ , is  $4PbO, C_{24}H_{20}O_{20}SO_3$ . The sulphosaccharic acid is easily separated by decomposing the sulphosaccharate of lead, suspended

in water, by sulfhydryc acid; but it is not very fixed, and is easily decomposed by a slight elevation of temperature.

Grape-sugar forms a crystallizable compound with sea-salt, obtained by dissolving in water 6 parts of sugar and 1 of salt, and allowing the liquid to evaporate spontaneously, when beautiful well terminated crystals are deposited, of which the formula is  $\text{NaCl}, 2(\text{C}_{12}\text{H}_{12}\text{O}_{12}) + 2\text{H}_2\text{O}$ . In a dry vacuum, or under the influence of heat, these crystals part with 2 equivalents of water and fall to dust.

§ 1295. A boiling solution of grape-sugar reduces immediately the blue liquor obtained by pouring potassa and tartrate of potassa into salts of the oxide of copper  $\text{CuO}$ , and precipitates from it the red suboxide of copper  $\text{Cu}_2\text{O}$ ; which reaction is extremely sensible, because these cupreous compounds possess considerable colouring power; and it enables the chemist to detect the presence of very small quantities of sugar in a liquor, besides affording an easy means of distinguishing grape-sugar from cane-sugar, which produces no similar effect.

It has been proposed to apply this reaction to the purpose of ascertaining the quantity of grape-sugar existing in a fluid. The cupreous liquor is prepared by dissolving together sulphate of copper, tartrate of potassa, and caustic potassa, which produce an intensely blue liquor; after which the solution is reduced to a certain standard, such, for example, that 100 cubic centimetres of it shall be exactly discoloured when boiled with 1 gm. of grape-sugar.\* In order to use the standard solution, 100 cubic centimetres of it are boiled in a porcelain capsule, and the liquor to be tested is gradually added to it by means of an alkalimeter. The volume of liquor which produces the exact effect contains precisely 1 gm. of sugar.

This process will also serve to determine the quantity of cane-sugar contained in a liquid, as it suffices to convert the sugar, by boiling it with an acid, into sugar turning to the left, which produces the same effect on the cupreous liquid, and then to operate with this liquid as has been stated, after having saturated the excess of acid.

Lastly, the process may also be applied to the determination of the proportions of cane-sugar and grape-sugar which may be mixed, by first ascertaining the discolouring power of a simple solution of

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\* The solution which has been found most efficient is prepared by first dissolving 20 gm. sulphate of copper in 80 cubic centimetres of water; and then adding 343.8 gm. of a solution of caustic potassa, of the specific gravity 1.12, to a solution of 80 gm. neutral tartrate of potassa in 80 cubic centimetres of water. Mix the two solutions by pouring the cupreous solution into the alkaline liquid, by small quantities at a time, and dilute the whole to the volume of 1 litre. When thus prepared the solution will keep unchanged for years.—*W. L. F.*

the mixture, and then that of an equal quantity of the mixture after the cane-sugar has been changed by boiling with an acid.\*

#### GELATINOUS PRINCIPLES OF FRUITS.

§ 1296. The juices of all ripe fleshy fruits yield, by continued boiling under certain conditions, gelatinous substances, which are derived from an immediate principle, insoluble in water, which exists in greater or less proportion in all vegetables, and to which the name of *pectose* has been given.

Pectose, which is chiefly found in the pulp of unripe fruits and certain roots, such as carrots and turnips, is intimately mixed with the cellulose which composes the cells. As it is entirely insoluble in water and all other solvents, and moreover very easily changeable, it has hitherto not been isolated, and its chemical composition has not been ascertained; but we are led to admit its existence from the peculiar products which it affords under the influence of various

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\* By measuring the deviations produced on the plane of polarization, the quantity of cane-sugar contained in solutions can be ascertained with great exactness, when the liquid to be tested contains no other principles which cause the plane of polarization to deviate.

For this purpose a preparatory experiment is made, on a known weight, for example, 20 gm. of very pure cane-sugar, by dissolving them in a quantity of water such that the solution shall occupy a given volume, which we will call V, and using of this solution as much as is necessary to fill a tube the constant length of which shall be, for example, 0.3 m.: let N be the deviation observed through the tube, under these circumstances. On now making, with other weights of the same sugar, solutions of equal volume V, and filling the same proof-tube with them, they will produce deviations  $n$ ,  $n'$ ,  $n''$ , and the weight of sugar contained in the volume V of these solutions will be respectively  $20 \text{ gm. } \frac{n}{N}$ ,  $20 \text{ gm. } \frac{n'}{N}$ ,  $20 \text{ gm. } \frac{n''}{N}$ , etc. From this, if the sugar thus tested be impure, but only mixed with substances deprived of the rotatory power, the same products  $20 \text{ gm. } \frac{n}{N}$ , etc., will express the *absolute* weight of pure sugar contained in the *gross* weight used to form V.

Tubes of different lengths may also be used, and the deviations observed reduced by calculation to that which they would have been if they had been measured in the same tube.

As the sugar of acid fruits turns the plane of polarization to the left, the quantity of this sugar formed, either in its artificial solutions or in the juices of fruits which do not contain other substances acting on the plane of polarization, may be ascertained by analogous processes; the molecular rotatory power of the fruit-sugar, or the deviation produced in the tube of 0.3 m. by the solution containing 20 gm. of the sugar in a volume of 100 cub. cent., having been equally determined *à priori*. It is necessary to operate always at the same temperature, for the molecular rotatory power of this kind of sugar varies considerably with the temperature.

The crystalline sugar of grapes and glucose turn the plane of polarization toward the right; and the preceding methods are therefore applicable to the determination of those sugars which exist in solutions containing no other active ingredients.

When cane-sugar is mixed with the sugar of acid fruits it is evident that the deviation  $n$  observed is only the difference between the deviation  $n'$  to the right of cane-sugar, and the deviation  $n''$  to the left of the sugar of acid fruits; but even in this case the quantities of the two species of sugar which exist in the solution can

chemical agents. The characteristic property of pectose is that of being transformed, under the simultaneous influence of acids and heat, into a substance soluble in water, and called *pectin*, which distinguishes pectose from cellulose, as the latter yields no similar product.

Pectin, which is found ready formed in ripe fruits, is developed in green fruits by the action of heat, their pectose being converted into pectin by the vegetable acids which they contain. Pectin is also obtained by boiling carrots and turnips with feebly acidulated water; but the most simple process consists in extracting it from ripe fruits. By expressing, for example, the pulp of ripe pears, and, after having filtered the juice, adding carefully oxalic acid, which precipitates the lime, and then a concentrated solution of tannin, which precipitates the albuminous matter, and, lastly, by pouring in alcohol, the pectin is precipitated in the form of long gelatinous filaments. This, being washed with alcohol and redis-

be determined. After having measured the deviation  $n$  produced by the mixed solution, exactly  $\frac{1}{10}$  of its volume of chlorohydric acid is added, and the liquid, having been well mixed, is maintained for 10 minutes at a temperature of  $140^\circ$  or  $150^\circ$ , by which means the cane-sugar is entirely changed into sugar turning to the left. After having reduced the temperature to exactly  $59^\circ$ , the deviation  $n$  of the new solution is again observed; and it now consists of the deviation  $n'$  of the original sugar of the acid fruits, and the deviation  $n''$  of the inverted sugar produced by the cane-sugar. But the state of saturation of the liquor has been changed by the addition of the chlorohydric acid, and in order to take it into account, the deviation observed  $n'$  must be replaced by the deviation  $\frac{1}{9}n$ , which would have been observed had it not been necessary to add the acid in order to produce the inversion. We have evidently, by admitting that a quantity of cane-sugar producing a deviation  $n'$  to the right yields a quantity of fruit-sugar deviating by  $Kn'$  to the left,

$$\begin{aligned} n &= n' - n'' \\ \frac{1}{9}n_1 &= n'' + Kn'; \end{aligned}$$

which two equations will serve to determine the unknown deviations  $n'$  and  $n''$ , from which may be calculated the proportions of the two kinds of sugar. The proportional coefficient  $K$  is determined, once for all, by a first experiment, made with very pure crystallized cane-sugar, at the temperature at which the test is to be made.

If the cane-sugar were mixed with grape-sugar or glucose, the solution of the solution  $n$  would still be observed, and would be the sum of the separate rotations  $n'$  and  $n''$  of the cane-sugar and glucose. By then heating the liquor with  $\frac{1}{10}$  of its weight of chlorohydric acid, the cane-sugar alone would be changed into sugar turning to the left, while the glucose would remain unchanged. Supposing  $n'$  to be the rotation of the new liquor in a tube of the same length, there would exist for the determination of the unknown  $n'$ ,  $n''$  the two equations

$$\begin{aligned} n &= n' + n'' \\ \frac{1}{9}n_1 &= n'' - Kn'. \end{aligned}$$

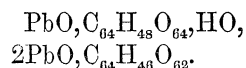
If the glucose were mixed with fruit-sugar the problem would be undetermined, because neither of these substances could be inverted in its action on the plane of polarization.

These methods may be successfully used to determine in solutions several other substances which turn the plane of polarization, and to study in these substances chemical phenomena which are with difficulty explained by ordinary chemical experiments.

solved in water, is again precipitated by alcohol and dissolved in water, which processes are repeated until reagents no longer indicate the presence of sugar or any organic acid.

Pectin thus obtained is an uncrystallizable white substance, though soluble in water, from which alcohol precipitates it in a jelly; or, when this solution is somewhat concentrated, in the shape of long filaments. Pectin behaves like a neutral substance to coloured reagents, and is not precipitated by the neutral acetate of lead, while the subacetate, on the contrary, throws it down from its solutions in combination with the oxide of lead. It exerts no action on polarized light; and its composition corresponds to the formula  $C_{64}H_{48}O_{64}$ .

An aqueous solution of pectin is converted, by boiling for several hours, into a new white substance, called *parapectin*, presenting the same chemical composition as pectin, and, being neutral with coloured reagents, very soluble in water, uncrystallizable, and insoluble in alcohol, which precipitates it in a transparent jelly. It therefore closely resembles pectin, but is distinguished from it by being precipitated by neutral acetate of lead. The composition of parapectin, dried at  $212^{\circ}$ , is the same as that of pectin; but it affords two compounds with oxide of lead, which are obtained by precipitating its solutions by the neutral acetate and subacetate. The formulæ of these compounds are



Parapectin, when heated to ebullition with very dilute acids, is converted into a new isomeric modification, called *metapectin*; which is distinguished from pectin and parapectin by sensibly reddening the tincture of litmus, and, being precipitated by chloride of barium; properties possessed neither by pectin nor parapectin. Metapectin is soluble in water and uncrystallizable. It is precipitated by alcohol, and combines with acids, forming compounds soluble in water, but precipitable by alcohol.

Pectin, parapectin, and metapectin are converted into an insoluble acid, called *pectic acid*, by contact with the alkalies and alkaline earths.

§ 1297. The vegetable parts which contain pectose, contain also a peculiar substance called *pectase*, which exerts quite a special influence on pectin and its isomerics, analogous to that of beer-yeast on sugars. This substance may be separated by precipitating the juice of fresh carrots by alcohol; and after the precipitation the pectase has become insoluble in water, without losing its power of action on pectin.

Pectase possesses the remarkable property of transforming, in a short time, pectin into a gelatinous substance, insoluble in cold water, without any apparent chemical intervention of its elements in the transformation. This phenomena, which is called *pectic fermenta-*

tion, resembles other phenomena of fermentation, which shall soon be described in detail. The reaction may be effected when protected from the air, is accompanied by no evolution of gas, and is particularly easily performed at the temperature of  $86^{\circ}$ .

Pectase is uncrystallizable, and, when left in water for 2 or 3 days, decomposes rapidly, becoming covered with mould, and no longer acting as pectin leaven. Its action on pectin is also destroyed by heating it for some time in boiling water. Pectase exists in vegetables, sometimes in its soluble and sometimes in its insoluble modification; while acid fruits, on the contrary, contain it only in its insoluble modification.

§ 1298. By introducing pectase into a solution of pectin, the latter is converted into an acid called *pectosic acid*, very slightly soluble in cold water, and which is precipitated in the gelatinous state. The acid is also obtained by causing cold and very dilute solutions of potassa, soda, ammonia, or the alkaline carbonates, to act on pectin; when pectosates are formed, from which the pectosic acid may be precipitated by an acid. It is essential that the alkaline liquids should not be concentrated, nor act for too long a time, for the pectosic acid would be transformed into a new acid, called pectic.

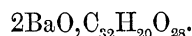
Pectosic acid is gelatinous, almost insoluble in cold, but soluble in boiling water; and the solution made when hot becomes gelatinous on cooling. Pectosates are gelatinous and uncrystallizable; and the formula of the lead-salt is  $2\text{PbO}, \text{C}_{32}\text{H}_{21}\text{O}_{29}$ .

§ 1299. If the action of pectase on pectin be continued for a sufficient length of time, the latter is converted first into pectosic and then into pectic acid; which latter transformation pectin also undergoes when it is treated with dilute solutions of the alkalies or alkaline carbonates, or with lime and baryta. By treating the pectosates with chlorohydric acid, the pectic acid is precipitated.

Pectic acid is generally obtained from carrots or turnips, by washing the pulp of the roots until the water is colourless and tasteless; after which it is heated for 15 minutes with a weak solution of carbonate of soda, which converts the pectin into pectic acid, forming a soluble pectate of soda. The liquor is separated, and chlorohydric acid added, which precipitates the impure pectic acid in the state of jelly. It is washed as completely as possible, and redissolved in ammonia; and, after boiling the liquid, a few drops of subacetate of lead are poured in, which precipitate a small quantity of pectic acid, with some albuminous matter which pertinaciously follows the pectic acid; after which the pectic acid remaining in the solution is precipitated by chlorohydric acid.

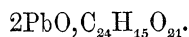
Pectic acid is quite insoluble in cold, and nearly so in boiling water, which distinguishes it from pectosic acid, which dissolves, on the contrary, largely in hot water. Pectic acid dissolves readily in alkaline solutions, even when very dilute. The pectates of the alkalies and that of ammonia alone are soluble, while all other pec-

tates are insoluble, and precipitate in very voluminous gelatinous masses. No soluble pectate crystallizes, but remains, after evaporation, in the form of a gummy mass. It is very difficult to obtain well-defined salts, as the composition of those procured by double decomposition varies greatly with that of the soluble pectate and the circumstances under which the precipitation takes place. The formula of pectic acid has been deduced from the analysis of the pectate of baryta obtained by treating, when cold and protected from the air, a solution of pectin with a large excess of water of baryta, when at first a precipitate of pectosate of baryta forms, which, under the influence of the excess of base, is converted into pectate of baryta. The salt, first dried in vacuo, then in an air-bath at  $248^{\circ}$ , presents the composition



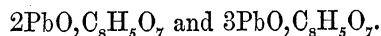
When pectic acid is boiled for a long time in water it dissolves in it completely; but is then converted into a new soluble acid, called *parapectic*. Pectates kept for a long time at a temperature of  $302^{\circ}$  are also changed into parapectates; the same transformation taking place as when their solutions are boiled for a long time.

Parapectic acid, which is very soluble in water and uncrystallizable, exerts an acid reaction on coloured tinctures, and forms soluble salts with potassa, soda, and ammonia; while its other salts are insoluble, and prepared by double decomposition. The formula of the parapectate of lead, dried at  $302^{\circ}$ , is



§ 1300. A solution of pectin left to itself for several days becomes strongly acid, and loses the property of being precipitated by alcohol; after which it contains a new acid, called *metapectic*; the transformation taking place much more rapidly in the presence of pectose, or the pulp of green fruits. Pectin undergoes the same changes in a very short time, when boiled with dilute acids, or with slightly concentrated alkaline solutions; and lastly, pectic and parapectic acids are converted into metapectic acid when they are boiled with dilute acids, and even undergo this change, after a length of time, in cold water.

Metapectic acid, which is very soluble in cold water, is uncrystallizable, and forms soluble salts, which do not crystallize, with a great number of bases. Its solutions are not precipitated by waters of lime and baryta, but they afford precipitates with the subacetate of lead. Two metapectates of lead are known, of which the formulæ are



Metapectic acid is as powerful an acid as the majority of acids found in fruits.

At the boiling point, parapectic and metapectic acids decompose the double tartrate of potassa and copper, and precipitate from it red suboxide of copper; in which respect they behave like grape-sugar, and sugar turning to the left; while these acids, like all the products derived from pectin, are distinguished from sugars by exerting no action on polarized light.

§ 1301. The following table shows the composition of the various substances derived from pectose, and exhibits the relations between their formulæ :

	Formula of the free substance.	Formula of the compound with oxide of lead.
Pectose.....	unknown,	unknown.
Pectin.....	$C_{64}H_{40}O_{56}, 8HO,$	unknown.
Parapectin.....	$C_{64}H_{40}O_{56}, 8HO,$	$PbO, C_{64}H_{40}O_{56}, 7HO.$
Metapectin.....	$C_{64}H_{40}O_{56}, 8HO,$	$2PbO, C_{64}H_{40}O_{56}, 6HO.$
Pectosic acid.....	$C_{32}H_{20}O_{28}, 3HO,$	$2PbO, C_{32}H_{20}O_{28}, HO.$
Pectic acid.....	$C_{32}H_{20}O_{28}, 2HO,$	$2PbO, C_{32}H_{20}O_{28}.$
Parapectic acid.....	$C_{24}H_{15}O_{21}, 2HO,$	$2PbO, C_{24}H_{15}O_{21}.$
Metapectic acid.....	$C_8H_5O_7, 2HO.$	$2PbO, C_8H_5O_7.$

From this manner of writing the formulæ, it will be seen that they are all multiples of the most simple formula,  $C_8H_5O_7$ , if certain quantities of hydrogen and oxygen be neglected, which we have separated from the formulæ, as if they existed in the state of water. If these relations are correct, it may be said that all the substances are derived from the first, pectin, by simple molecular partitions, and by separations or absorptions of water. Pectin is a neutral substance, and in its modifications acquires more and more decided acid properties, the last transformation being an acid as powerful as the majority of those of the vegetable kingdom. But it is important to remark that the determination of the formulæ of uncrystallizable substances as unstable as those first described, and of which the acid properties are so slightly marked, presents great difficulties, and too much importance must not be attached to them.

§ 1302. The successive transformations of pectin under the influence of pectase and the acids explain readily the modifications of this substance during the ripening of fruits, and during the process of cooking which yields jellies.

Vegetable jellies are produced by the transformation of pectose or pectic acid under the influence of pectase, which transformation most frequently stops at pectosic acid; for jellies generally disappear when they are heated to  $212^\circ$ , because the pectosic acid is then dissolved; while the syrupy juice again sets into a jelly on cooling, on account of the separation of gelatinous pectosic acid. It must be admitted that, under the influence of heat and the vege-



table acids which exist in the pulp, pectose is first converted into pectin, and that the latter, under the influence of pectase, is converted into pectosic acid; and that it may even be changed into pectic acid if the action of the pectase be sufficiently prolonged. It is important to raise the temperature slowly, because, if the fruit were suddenly exposed to a temperature of  $212^{\circ}$ , the action of the pectase would be paralyzed, and the pectic fermentation would no longer be produced; which happens in preserving fruits: they are dipped only for a few moments in boiling water, and the pectase is thus rendered inactive.

*Mannite*  $C_6H_7O_6$ .

§ 1303. Mannite, which is a substance widely scattered through the vegetable organization, exists in the proportion of 60 per cent. in manna, the dried juice which flows spontaneously from certain species of ash-trees in the south of Europe, and from which mannite is easily extracted by boiling it with concentrated alcohol, which dissolves the mannite and again deposits it on cooling. Mannite also exists in the juice of onions, asparagus, celery, and mushrooms, together with sugar and other soluble vegetable substances, and is obtained from them by first destroying the sugar by fermentation, which does not alter the mannite, and then evaporating the liquor to dryness and treating it with boiling alcohol, which dissolves the mannite. The juice of sugar-beets, which after fermentation contains a large quantity of mannite, is evaporated to the consistence of syrup, and treated with alcohol to dissolve the mannite.

Mannite, crystallized in alcohol, presents the appearance of long acicular crystals: it dissolves in 5 parts of cold, and in a smaller quantity of boiling water; and its aqueous solution, slowly evaporated, yields larger and better-defined prismatic crystals. Heated slightly above  $212^{\circ}$ , it melts into a colourless liquid which, on cooling, assumes a crystalline texture; but if heated still further, it is decomposed and yields products analogous to those of the sugars.

Mannite is distinguished from the sugars by exerting no rotatory power on polarized light, by yielding no sugar turning to the left when treated with acids, and by not fermenting by contact with the leaven of sugar-like substances. Fuming nitric acid transforms it into an explosive substance, resembling that produced under the same circumstances by lignin, starch, and sugar; while the nitric acid of commerce yields, when hot, oxysaccharic and oxalic acids. The formula admitted for mannite is  $C_6H_7O_6$ , but it should be probably doubled or trebled.

Mannite combines with oxide of lead, when a very concentrated aqueous solution of it is poured into a hot solution of ammoniacal acetate of lead; when the compound separates, on cooling, into small crystalline lamellæ of the formula  $2PbO, C_6H_5O_4$ . The com-

position of this product indicates that the formula of mannite should be written  $C_6H_5O_4, 2HO$ .

PRODUCTS OF THE ACTION OF ACIDS ON LIGNIN, CELLULOSE,  
AMYLACEOUS MATTER, AND THE SUGARS.

ACTION OF DILUTE ACIDS ON STARCH.

*Dextrin*  $C_{12}H_{10}O_{10}$ .

§ 1304. It has been mentioned (§ 1283) that fecula, when boiled for some time with water containing some hundredths of sulphuric acid, is soon completely dissolved, being first converted into a substance closely resembling gum arabic, and then, if the ebullition be continued, changing into a sugar turning the plane of polarization of polarized light to the right. The first product of transformation of the amylaceous matter has received the name of *dextrin*, because it possesses the property of deviating polarized light more powerfully to the right than any other known substance. As the elementary composition of dextrin is the same as that of amylaceous matter, this transformation can only be owing to disaggregation; the sulphuric acid by which it has been effected being found unchanged in the liquid.

Dextrin is very soluble in water, and dissolves also in dilute alcohol, but is insoluble in absolute alcohol. As it dissolves but sparingly in concentrated alcohol, which dissolves a much larger proportion of sugar turning to the left and grape-sugar, this solvent is frequently employed to separate dextrin from those sugars with which it is ordinarily mixed when prepared by the process just indicated. Dextrin separated from its solutions by evaporation assumes the form of a colourless, transparent substance, without any appearance of crystallization, closely resembling gum arabic, but possessing an opposite rotatory power. Heated with the nitric acid of commerce, it yields oxalic acid, but not mucic acid, thus distinguishing it chemically from the gums. Iodine does not colour solutions of dextrin, which affords an easy method for ascertaining when the transformation of the amylaceous matter is completed, and which exhibits the action of sulphuric acid in the preparation just indicated. By pouring into a small quantity of the hot liquor, previous to boiling, a few drops of an aqueous solution of iodine, the beautiful indigo-blue colour peculiar to the pure amylaceous matter is produced; while, if the same experiment be repeated some time after, the iodine produces a violet tinge, and, at a still later period, a purplish or reddish hue: lastly, no change of colour is effected; the yellowish tinge being merely due to the aqueous solution of iodine. But at this period a portion of the dextrin formed has generally undergone a more advanced transformation, and is changed

into sugar turning to the right, but of which the rotatory power is less than its own.

Solutions of dextrin possess some properties of solutions of gum, and may be substituted for them occasionally in the arts.

One method of preparing dextrin consists in heating fecula to a temperature of about  $410^{\circ}$ , when it becomes disaggregated and converted into dextrin; the dried fecula being spread in layers of 3 or 4 centimetres in thickness, on sheet-iron tables in a furnace heated by a regular circulation of hot air, the temperature of which must not exceed  $410^{\circ}$ .

The product thus obtained is called *torrefied starch*, or *leïocomme*, and exhibits the pulverulent appearance of fecula, while its colour is slightly yellowish, owing to a more advanced decomposition.

Another process consists in moistening 1000 kilogs. of fecula with 300 of water, containing 2 kilogs. of nitric acid, and, after allowing the substance to dry spontaneously, heating it for 1 or 2 hours in a stove at  $212^{\circ}$  or  $230^{\circ}$ ; when the transformation is perfected and the acid is evaporated.

§ 1305. *Diastase*.—A peculiar nitrogenous substance, called *diastase*, which possesses the property of converting a large proportion of fecula into dextrin, and even into sugar when its action is sufficiently prolonged, exists in the germ of the cerealia and tubercular vegetables. It appears to be formed at the moment of germination, probably at the expense of the albuminous matter contained in the grain, as it resides in the very origin of the germ, and in the eye of the tuber; and its use in the vegetable economy appears to be that of disaggregating the amylaceous matter and transforming it into an isomeric soluble substance, which the vital forces then change into other isomeric, but insoluble substances, such as cellulose, which is to form the frame-work of the growing plant.

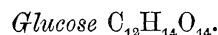
Diastase is generally extracted from barley which has sprouted, by digesting the powdered grain in water at  $77^{\circ}$  or  $86^{\circ}$ , and, after several hours, compressing the paste in a cloth and filtering; when the liquid contains diastase in solution, and may be used immediately to effect the solution of starch. If the active principle is to be separated from it, it must be heated to  $167^{\circ}$ , a temperature which does not alter the diastase, but at which an albuminoid substance mixed with it coagulates. Anhydrous alcohol is then poured into the liquor as long as any precipitate is formed, when the diastase is precipitated in flakes, which are redissolved in water and again precipitated by alcohol. The substance, dried in vacuo, is white, amorphous, soluble in water and weak alcohol, but insoluble in concentrated alcohol. The aqueous solution is neutral and tasteless, and is not precipitated by acetate of lead. Diastase may be preserved for a long time in dry air, but soon putrefies in dampness; and a temperature of  $212^{\circ}$  deprives it entirely of its action on starch, which is very powerful, for 1 part of diastase is sufficient to trans-

form into dextrin, and subsequently into sugar, 2000 parts of fecula; to produce which effect by the action of acid, it would require 30 times the weight of sulphuric acid. It cannot be supposed, on account of the small proportion of diastase, that any ordinary chemical reaction takes place; and the phenomenon must rather be compared to those mysterious actions, called *actions by contact*, of which several examples have been pointed out in mineral chemistry; and it may also be assimilated to other phenomena, also imperfectly explained, known by the name of *fermentation*, of which we have seen the first instance in the action of pectase on pectin.

Diastase appears to be most active between the temperatures of  $149^{\circ}$  and  $167^{\circ}$ , the action ceasing at a higher degree. At  $32^{\circ}$  it still converts starch into dextrin and sugar, but at  $10.4^{\circ}$  dextrin only is formed. Diastase exerts no action on cellulose, lignin, nor even on cane-sugar, which is so easily changed by dilute acids.

The action of diastase is likewise applied in the arts to the purpose of obtaining dextrin with more or less sugar, the transformation being effected in a double boiler, between the sides of which steam is made to circulate. The ground barley, called *malt*, being suspended in water heated to  $167^{\circ}$ , the fecula is added to it by small quantities as it dissolves. The operation is watched, and the liquor tested from time to time with the aqueous solution of iodine, and, when a vinous colour is produced, the action of the diastase must be quickly paralyzed, as, otherwise, a large quantity of sugar would be formed; and it is done by rapidly heating the liquor to  $212^{\circ}$ , by passing steam through it. It is then decanted and evaporated to the consistence of syrup.

The dextrin thus prepared is used in the baking of pastry, or in the manufacture of beer, cider, alcohol, and various other alcoholic liquors; while that arising from the torrefied fecula, or the action of acids, is used in the finishing of muslins, the thickening of mordants in dyeing and calico printing and wall-paper printing, etc. etc. Of later years it has been used in surgery, in what is called the immovable treatment of fractures:—Muslin bandages, soaked in a mucilaginous preparation, obtained by dissolving 100 gm. of dextrin in 50 of camphorated brandy, and adding, soon after, 40 gm. of water, are rolled around the limb, and the apparatus becomes immovable when the dextrin is dry. They are easily removed, when necessary, by softening the dextrin with warm water.



§ 1306. If the action of diastase, or that of the acids on starch, be prolonged, the dextrin which is first formed is converted into sugar; and the solution, when evaporated, sets into a crystalline mass resembling that formed by grape-sugar. This sugar is called *glucose*, and its identity with grape-sugar is generally admitted. In the transformation the amylaceous matter  $C_{12}H_{10}O_{10}$  absorbs 4 equiv.

of water to constitute glucose  $C_{12}H_{22}O_{11}$ ; and it is important to remark that cane-sugar  $C_{12}H_{22}O_{11}$  is intermediate between these two substances, while it has hitherto been impossible to arrest the absorption of water at 1 equiv.; for it would be of immense commercial value if the intermediate product were cane-sugar, which is much more valuable than glucose.

Glucose is found in commerce under three different forms: syrup of fecula, glucose in mass, and granulated glucose.

The saccharification is generally effected by sulphuric acid, diluted with 33 times its weight of water, and heated to a temperature slightly above  $212^{\circ}$ , the operation being performed in large wooden tubs, at the bottom of which a leaden tube, having a great number of holes, is placed. The tube may be made to communicate with a high pressure steam-generator, which drives steam immediately into the water in the tub, which, being  $\frac{2}{3}$  filled with acidulated water, is thus rapidly heated to  $212^{\circ}$ . The fecula previously diluted with water is gradually added, and in 30 or 40 minutes after the last addition of fecula the conversion into sugar is completed. In order to ascertain this, a few drops of the liquid are allowed to cool on a plate, and then treated with a small quantity of a solution of iodine, which should produce no change of colour. When this result is obtained, the flow of steam is arrested, and the acid is saturated with powdered chalk, which should be gradually added, lest the effervescence produced should cause the liquid to overflow; and the moment of saturation is ascertained by means of the tincture of litmus. The liquor is allowed to rest for 12 hours, after which it is decanted and bleached by filtration through animal black, and it is then evaporated in order to reduce it to the degree of concentration required. If solid glucose is to be obtained, the syrup is concentrated until it marks  $40^{\circ}$  or  $42^{\circ}$  of Baumé, and then, when sufficiently cool, it is run into barrels, in which it solidifies. In order to granulate it, it is evaporated to only  $32^{\circ}$  B., and then allowed to remain for 24 hours in reservoirs, in which it cools as rapidly as possible, while the calcareous salts are deposited; after which the syrup is brought into vats, the bottoms of which are pierced with small holes closed with pins; fermentation being prevented by pouring into each vat 2 decilitres of an aqueous solution of sulphurous acid. Crystallization does not commence for 8 days: when  $\frac{2}{3}$  of the mass are solidified the pins are removed and the liquid flows out. The crystals are then dried on cakes of plaster, in a drying machine, of which the temperature should not exceed  $77^{\circ}$ , in order to prevent the fusion of the grains.

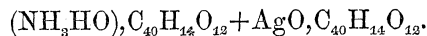
Glucose in grains is rarely made, except for the purpose of adulterating brown sugar.

Glucose, in syrup or in bulk, is used in the manufacture of beer and alcohol, and for the improvement of common wines.

## ACTION OF ACIDS ON SUGARS.

§ 1307. It has been mentioned that cane-sugar, by being boiled with acids, is readily converted in sugar turning to the left, which itself, after some time, undergoes a change, and separates from its solutions in the form of grape-sugar or glucose. If the action of the acids be continued, and especially if they be highly concentrated, the reactions produced are much more complicated. Fruit-sugar and glucose should, moreover, evidently yield the same products.

On dissolving 100 parts of cane-sugar in 300 parts of water, to which 30 parts of sulphuric acid are added, and heating the liquor, it will soon be seen to turn brown. The new products formed vary with the temperature of the liquor; and if the experiment be made in a retort communicating with a receiver in which a vacuum has been effected, the liquor boils at a low temperature; while if the operation be arrested after the distillation of a portion of the water, the residue is found to contain glucic acid, in larger quantity according to the prolongation of the action; besides a small quantity of apoglucic acid. If, on the contrary, the liquor be boiled, under the pressure of the atmosphere, after having previously filled the apparatus with carbonic acid or hydrogen gas, in order to prevent the oxygen of the air from affecting the reaction, it turns brown, and soon deposits black flakes, formed by the admixture of two new substances, *ulmin* and *ulmic acid*. These substances are separated by means of potassa, which forms a soluble salt with ulmic acid, while the ulmin is isolated. The formula of ulmin, dried at  $284^{\circ}$ , is  $C_{40}H_{16}O_{14}$ ; and the solution of ulmate of potassa, which is of a deep red colour, deposits, when saturated with an acid, ulmic acid in the form of a gelatinous black precipitate. The acid is slightly soluble in fresh water, but does not dissolve in water containing acids or salts. The composition of ulmic acid, dried at  $284^{\circ}$ , is the same as that of ulmin, but at  $383^{\circ}$  it loses 2 equivalents of water without further change, and takes the formula  $C_{40}H_{14}O_{12}$ . The acid dried at  $284^{\circ}$  is therefore a hydrate  $C_{40}H_{14}O_{12} + 2HO$ . By dissolving ulmic acid in ammonia, a soluble salt is obtained, of the formula  $(NH_3, HO), C_{40}H_{14}O_{12}$ ; and by pouring soluble metallic salts into a solution of ulmate of ammonia, double ammoniacal ulmates are precipitated. Thus, the formula of the precipitate yielded by nitrate of silver is



The water which distilled over during the ebullition of the sugar with sulphuric acid contains a certain quantity of formic acid  $C_2HO_3, HO$ ; the production of which, being rich in oxygen, explains how sugar, in which oxygen and hydrogen exist in quantities forming water, yields, in this new reaction, substances in which hydrogen predominates. If the contact of air is not avoided in this ex-

periment, or better still, if the boiling be effected in glass vessels, the ulmin and ulmic acid undergo new transformations, which, to be perfect, require a prolonged action of the sulphuric acid, which is still further concentrated by evaporation: two black substances, *humin*, and *humic acid*, are formed, and are separated by potassa, which dissolves the latter. The formula of humin is  $C_{40}H_{15}O_{15}$ , and that of humic acid  $O_{40}H_{12}O_{13}$ ; and these substances are therefore derived from ulmin and ulmic acid by simple oxidation. The formula of hydrated humic acid is  $C_{40}H_{15}O_{15}$ , showing it to be isomeric with humin; but as it loses 3 equivalents of water by heat, its formula should be written  $C_{40}H_{15}N_{12} + 3HO$ . In fact, the formula of the humate of silver, dried at  $212^{\circ}$ , is  $AgO, C_{40}H_{15}O_{13}$ .

When the action of acids is continued for a long time, and especially when the humin and humic acid are boiled with concentrated chlorohydric acid, formic acid is again disengaged, and a black substance is obtained, the composition of which, dried at  $293^{\circ}$ , corresponds to  $C_{34}H_{13}O_9$ . The same substance is formed when humin and humic acid are boiled with a concentrated solution of caustic potassa, and the residue of evaporation is heated to  $572^{\circ}$ . When the action of the caustic potassa is continued, raising the temperature more and more, there are successively formed two new substances, insoluble in potassa, the formula of the first of which is  $C_{34}H_{10}O_6$ , and that of the second  $C_{34}H_7O_5$ . By comparing the formula of these compounds, it will be observed that the potassa immediately effects the separation of new quantities of water.

#### ACTION OF SULPHURIC ACID ON CELLULOSE.

§ 1308. Cellulose dissolves readily in cold concentrated sulphuric acid, being first converted into dextrin, and then into glucose. The experiment is made by wetting 2 parts of old linen, or paper, with 3 parts of concentrated sulphuric acid, digesting the mixture for several hours, and treating the gummy matter, which remains perfectly colourless, with water. The sulphuric acid is then saturated with carbonate of baryta, and filtered, when the liquor contains dextrin, and a very small quantity of a soluble salt of baryta, formed by a peculiar acid containing sulphuric acid. If, on the contrary, the mixture be boiled for several hours with water, the dextrin is completely converted into glucose, and a weight of this sugar may be obtained greater than that of the linen used in the experiment; which result is explained by the formulæ of the two substances; that of cellulose being  $C_{12}H_{10}O_{10}$ , while that of glucose is  $C_{12}H_{14}O_{14}$ ; showing that the cellulose combines with water to form glucose.

Starch, inulin, and the gums likewise dissolve in cold concentrated sulphuric acid, and are converted into products analogous to those yielded by cellulose.

ACTION OF NITRIC ACID ON CELLULOSE, AMYLACEOUS MATTER,  
DEXTRIN, AND SUGARS.

§ 1309. The concentrated nitric acid of commerce acts energetically, when hot, on all these substances, first dissolving them, and then giving off nitrous vapours; while, if the operation be sufficiently prolonged, the liquid is found to contain only oxalic mixed with an excess of nitric acid. It has been mentioned (§ 259) that this is one way of preparing oxalic acid. But by using more dilute nitric acid, and heating it in a water-bath, a new acid, which has been called *oxysaccharic*, and sometimes *oxalhydric acid*, is first formed; the best method of obtaining which consists in heating in a water-bath 1 part of cane-sugar dissolved in a large quantity of water, with 2 parts of nitric acid. When the evolution of nitrous vapours ceases, the liquor is saturated with chalk, and then filtered to separate the oxalate of lime and chalk in excess; after which acetate of lead is added, which throws down a white precipitate of oxysaccharate of lead. The precipitate is suspended in water, and decomposed by a current of sulfhydric acid gas, which precipitates sulphide of lead, while the oxysaccharic acid remains isolated in the liquor. This is divided into 2 equal parts, one of which being exactly saturated by carbonate of potassa, the other half is added to it; by which means a binoxysaccharate of potassa is produced, a salt which crystallizes readily, and may be purified by successive crystallizations. It is easy to prepare oxysaccharic acid by means of this salt, by again precipitating it by acetate of lead, and decomposing the salt of lead by sulfhydric acid.

Oxysaccharic acid is very soluble in water, and has never been obtained in a crystalline form.

The binoxysaccharate of potassa, which dissolves in 4 parts of boiling water, but is very slightly soluble in cold water, has the formula  $(KO+HO), C_{12}H_8O_7$ .

The formula of oxysaccharate of zinc is  $2ZnO, C_{12}H_8O_7$ , showing the acid, therefore, to be bibasic, (§ 1225.)

Nitric acid readily converts oxysaccharic into oxalic and carbonic acids.

§ 1310. Monohydrated nitric acid, when cold, exerts on starch, cellulose, and sugar—an action very different from that of the same acid when hot and more dilute; forming highly explosive, insoluble substances, which are suddenly converted into a gaseous volume 600 or 800 times larger than themselves. During the last few years, these substances have attracted considerable attention, as it was supposed that they could be substituted for gunpowder.

When cotton is dipped, for 12 or 15 minutes, into monohydrated nitric acid, it does not change its appearance, although it absorbs a certain quantity of the acid; but if it be washed and carefully dried, a substance retaining the appearance of cotton, but which suddenly deflagrates when touched with a burning coal, is obtained.



This substance has been called *gun-cotton*, *nitric cotton*, and *pyroxyl*. Its composition, from the most correct analysis, corresponds to the formula  $C_{24}H_{17}O_{17}, 5NO_5$ ; according to which, 2 equivalents of cellulose  $C_{12}H_{10}O_{10}$  have lost 3 equivalents of water and gained 5 of nitric acid.

Pyroxil is insoluble in water, alcohol, and acetic acid, but dissolves sparingly in pure ether, while a much larger proportion dissolves in ether to which a few hundredths of alcohol have been added; and it also dissolves slightly in acetic ether. When properly prepared, pyroxil explodes at a temperature of about  $338^\circ$ , and yields a mixture of oxide of carbon, carbonic acid, nitrogen, and vapour of water.

Hemp, flax, linen, paper, and, in short, all substances consisting of cellulose, yield analogous products, the inflammability and projectile force of which are, however, not the same, owing undoubtedly to the difference of cohesion of the cellulose in the original substance. Starch yields a similar product, called *nitric starch*, or *pyroxam*, the chemical composition of which appears to be the same as that of pyroxyl. But pyroxam is soon spoiled spontaneously, especially in a moist atmosphere.

It has been ascertained that a mixture of equal equivalents of monohydrated nitric acid and concentrated sulphuric acid can be advantageously substituted for pure monohydrated nitric acid. The cotton is dipped into it, withdrawn in 15 or 20 minutes, and compressed with a glass spatula so as to dry it as much as possible; after which it is washed several times, and carefully dried at a temperature not exceeding  $212^\circ$ .

Gun-cotton, when used in firearms, communicates to the ball the same initial force as four times the same weight of powder, and possesses in addition the advantage of not fouling the piece nearly so much. It is also more easily transported, and is not injured by moisture; but all these good qualities are more than counterbalanced by great disadvantages, which have led to its rejection, after numerous experiments in various countries. Its chief objection is its liability to burst the gun, and in all cases to strain it more than common powder. Its price is also six times greater than that of powder; and several serious accidents have occurred in its manufacture, which, however, might possibly be avoided by greater care.

Comparative experiments made in mining with gun-cotton and blasting-powder have proved the great superiority of the former; the explosive force of gun-cotton having been found to be 4 times that of blasting-powder; and still greater effect, with more economy, has been produced by adding  $\frac{8}{10}$  of its weight of nitrate of potassa to the pyroxyl.

§ 1311. A solution of gun-cotton in ether yields by evaporation a transparent substance insoluble in water, and adhering power-

fully to any bodies to which the ethereal solution is applied. This substance, called *collodion*, is now extensively used in surgery; and in its preparation the process just described for the manufacture of pyroxyl is slightly modified; the cotton being allowed to remain for 1 or 2 hours in a mixture of 3 parts of concentrated sulphuric acid and 2 parts of nitrate of potassa, and then washed and dried as usual; after which the product is treated with ether containing 6 or 8 hundredths of alcohol, which dissolves a portion of it. The syrupy solution, spread over the skin, leaves, after the evaporation of the ether, an impervious pellicle insoluble in water, and sufficiently adhesive to be advantageously substituted for the ordinary adhesive plaster sometimes called *court-plaster*.

## ACTION OF NITRIC ACID ON GUMS.

*Mucic Acid*  $C_6H_4O_7, HO$ .

§ 1312. Gums treated with hot nitric acid of commerce (§ 1287) yield, in addition to oxalic and carbonic acids, another, the *mucic*, which is very slightly soluble in cold water; and we have said before that the production of this acid established a ready distinction between gums, amylaceous matter, dextrin, and the mucilaginous and gelatinous principles of vegetables. A peculiar kind of sugar, called *sugar of milk*, is found in the milk of mammiferous animals, differing essentially from the various kinds of sugar hitherto described, and also yielding mucic acid with nitric acid. It is generally employed in the preparation of the acid, by boiling 1 part of powdered sugar of milk with 6 parts of ordinary nitric acid, and allowing the liquid to cool as soon as the nitrous vapours cease passing over, when the mucic acid is deposited in the form of small granular crystals. It is washed in cold and then dissolved in boiling water, from which the liquor deposits pure mucic acid on cooling. Mucic acid dissolves in 66 parts of boiling water, is almost insoluble in cold water, and reddens tincture of litmus. If a solution of it be rapidly evaporated, the substance undergoes an isomeric modification and becomes soluble in alcohol, which does not dissolve ordinary mucic acid; and the alcoholic solution deposits, by evaporation, flattened crystals which dissolve in 17 parts of boiling water. But this modification of mucic acid is not very fixed, being rapidly converted into ordinary mucic acid when its solutions are allowed to cool. The two modifications of mucic acid yield different salts; and those of the second modification, which are the more soluble, are converted, when cold, into salts of the first modification.

The alkaline mucates are but slightly soluble in cold water, and the other salts are insoluble. The formula of mucate of silver is  
VOL. II.—2 R

$\text{AgO}, \text{C}_6\text{H}_4\text{O}_7$ ; and the formula of crystallized mucic acid is  $\text{C}_6\text{H}_5\text{O}_8$ , which should perhaps rather be written  $\text{C}_6\text{H}_4\text{O}_7, \text{HO}$ .

Mucic acid, heated in a glass retort furnished with a receiver, is decomposed and yields, together with very complicated empyreumatic products and a residue of carbon, a new acid, called *pyromucic*, which is partly deposited in the form of crystals in the neck of the retort. By dissolving these crystals in the liquor collected in the receiver, evaporating it to dryness, and subjecting the residue to resublimation, purer pyromucic acid is obtained; and lastly, the acid is redissolved in water and purified by crystallization. Pyromucic acid, which is colourless, melts at about  $266^\circ$ , volatilizing at a higher degree, and dissolves in 26 parts of cold and 4 of boiling water. The alkaline pyromucates are very soluble in water, while those of the alkaline earths are very slightly so.

The formula of pyromucate of silver is  $\text{AgO}, \text{C}_{10}\text{H}_3\text{O}_5$ , and that of sublimed pyromucic acid is  $\text{C}_{10}\text{H}_3\text{O}_5 + \text{HO}$ .

#### PRODUCTS OF THE SPONTANEOUS DECOMPOSITION OF CELLULOSE AND OF THE OTHER ESSENTIAL PRINCIPLES OF VEGETABLES.

§ 1313. Vegetables decompose spontaneously when exposed to moisture and the oxygen of the atmospheric air, being converted into a brown substance called *humus*, or *mould*, the nature of which is very imperfectly known. Peat in an advanced stage of decomposition, as well as the decomposed ligneous substances found in the cavities of certain trees, contain the same substances. Four principal substances have been procured from it, which appear to be identical with those obtained by causing acids to act on sugar at the temperature of ebullition, and which we have designated by the names of *humic acid*, *ulmic acid*, *humine*, and *ulmine*; although they sometimes, indeed, present states of hydration differing from those of the analogous products prepared with sugar.

The formula of an ulmic acid obtained from a peat from Frise was  $\text{C}_{40}\text{H}_{16}\text{O}_{14} + 2\text{HO}$ , that is, it contained 2 equivs. of water more than the ulmic acid of sugar; and the composition of its ammoniacal salt was  $(\text{NH}_3, \text{HO}), \text{C}_{40}\text{H}_{16}\text{O}_{14}$ .

A black peat from Härlem (Holland) yielded a humate of ammonia  $(\text{NH}_3, \text{HO}), \text{C}_{40}\text{H}_{14}\text{O}_{13} + 3\text{HO}$ ; which retained its water at the temperature of  $284^\circ$ , which is not the case in the analogous salt prepared with the humic acid resulting from the decomposition of sugar.

#### MINERAL FUEL.

§ 1314. Enormous quantities of combustible substances, of immense importance in metallurgy and the various arts, are found in

the bosom of the earth. They are evidently produced by the decomposition of vegetables which grew in the vicinity, or the *debris* of vegetables carried down by rivers. Peat mosses exhibit, though on a smaller scale, an example of this formation; as they consist of innumerable herbaceous vegetables, spontaneously decomposed by the action of water and atmospheric air; and their various stages of alteration may be followed, from the perfectly herbaceous turf to the earthy turf presenting but few or no recognisable remains.

The vegetable structure is frequently perfectly preserved in the mineral combustibles of the tertiary formation, where pieces of wood, called *lignite*, are found still retaining their original form, but having become friable, and yielding a brown powder by pulverization.

In the mineral fuel of older formations, the vegetable structure has generally disappeared, and it forms black, brilliant, compact masses, of a schistose texture, yielding a black or more or less brown powder; it is called *pit-coal*, or *sea-coal*, and is rare in the secondary, but very abundant in the transition formation; in the upper stratum of which they are so frequent as to characterize them by the name of *coal formation*.

In the upper strata of the transition rocks the mineral fuel, which is sometimes called *anthracite*, is generally very compact, rich in carbon, difficult to ignite, and yielding but little volatile matter by calcination. Anthracite is sometimes, though rarely, found in the superior strata, and even in the secondary rocks.

Pit-coal of the coal formation yields on calcination a great quantity of volatile substances and inflammable gases, and experiences, prior to decomposition, an incipient fusion, while the coal remaining, or the *coke*, presents the appearance of a swollen or bloated mass. Although the structure of plants can no longer be recognised in certain combustible minerals, their vegetable origin is undoubted, for in the layers of schist or sandstone which bound the layers of coal, impressions of plants are frequently found, which are so distinct and clear as to enable the botanists to detect the family to which they belong, and thus, partly, to restore the flora of antediluvial epochs.

In the tertiary rocks a mineral fuel is also found, which is soft, or easily fusible, forming irregular masses, or a kind of strata, and presenting a bearing analogous to that of the lignites, while at other times they permeate layers of schist or sandstone belonging to various geological formations, and then seem to arise from the decomposition, by heat, of other combustible minerals contained in the earth. Some of these substances, which are called *bitumen*, contain a large amount of nitrogen, and are fetid, yielding, on distillation, considerable quantities of carbonate of ammonia. They appear to have been generated by the putrefaction of animal matter, chiefly by that of fishes, the impressions of which are frequently found in the neighbouring rocks.

§ 1315. Coals may be divided into five classes :

1. The anthracites.
2. *Fat and strong*, or *hard* pit-coal.
3. *Fat blacksmith's* or *bituminous* coal.
4. *Fat* coal *burning with a long flame*.
5. *Dry* coal *burning with a long flame*.

1. Calcination scarcely changes the appearance of anthracites, as their fragments still retain their sharp edges, and do not adhere to each other. They have a vitreous lustre, and their surface is sometimes iridescent, while their powder is black or grayish-black. They burn with difficulty, but generate a large amount of heat when their combustion is properly effected. In blast-furnaces anthracites require a great blast, and those only can be used which do not soon fall to powder, as otherwise the furnace would be speedily choked. We have seen (§ 1072) that anthracite is used in Wales for heating reverberatory furnaces ; and it is now proper to remark, that the flame produced by the combustible under these circumstances is not owing to the combustion of the volatile substances given off by the anthracite, but rather to the combustion of the carbonic oxide formed by the passage of air through a thick layer of fuel.

2. *Fat and strong*, or *hard* pit-coals, yields a coke with metallic lustre, but less bloated and more dense than that of blacksmiths' coals. They are more esteemed in metallurgic operations requiring a lively and steady fire, and yield the best coke for blast-furnaces. Their powder is brownish-black.

3. *Fat bituminous*, or *blacksmith's* coals, yield a very bloated or swollen coke, with metallic lustre, and are more highly valued for forging purposes, because they produce a very strong heat, and allow the formation of small cavities, in which the pieces to be forged can be heated. Blacksmith's coal is of a beautiful black colour, and exhibits a characteristic fatty lustre: its powder is brown. It is generally brittle, and breaks into cubical fragments, which adhere to each other in the fire.

4. *Fat* coals *burning with a long flame* generally yield a swollen, metalloid coke, less bloated, however, than that of blacksmith's coal. These coals are much esteemed in a reverberatory furnace, particularly when a sudden blast is required, as in puddling, and are also well adapted to domestic purposes, and are preferred for the manufacture of illuminating gas. They yield a good coke, but in small quantity, and their powder is brown.

5. *Dry* pit-coal *burning with a long flame* yields a solid, metalloid coke, the various fragments of which scarcely adhere to each other by carbonization. This coal is also applicable to steam-boilers, and burns with a long flame, which, however, soon fails, and does not produce the same amount of heat as the coals of the preceding class.

§ 1316. The elementary analysis of combustible minerals, which easily explains their various properties, and indicates the uses to which each is most applicable, is effected like that of organic substances, (§ 1210 *et seq.*;) but as coal is generally difficult to burn, it is necessary, at the close of the experiment by which the quantity of water and carbonic acid it contains is determined, to pass a current of oxygen gas through the tube, (§ 1211,) which burns the last particles of carbon. The organic analysis of coal yields the hydrogen, carbon, and nitrogen which they contain; but it is also necessary to determine the proportion of earthy matter which exists in very various degrees in them, and which remains in the ashes after combustion.

For this purpose two grammes of the coal are ignited in a thin platinum capsule, heated by an alcoholic-lamp, and the ashes remaining are weighed. This method of incineration is difficult, and requires considerable time, only in those anthracites which do not burn readily, and it is then more easily effected if the coarsely powdered anthracite be placed in a small platinum vessel, heated in a current of oxygen in a porcelain tube.

It is essential carefully to examine the nature of the ashes. Sea-coal of the coal formation frequently leaves argillaceous ashes, in which case there is a trifling error in the supposed composition of the fuel, because the small quantity of water always contained in clay, and which it loses at a red-heat, is regarded as existing in the state of hydrogen; and this error, which is of no importance if the quantity of ashes is small, may be considerable in the opposite case. The ashes often contain, likewise, peroxide of iron, which metal generally exists in coal in the state of pyrites, and the analysis is thus inaccurate for two reasons: the proportion of ashes is valued at too low a rate, because, instead of the iron pyrites, sesquioxide of iron is weighed, the weight of which, for the same quantity of iron, is less; and again, in combustion by oxide of copper, the substance may yield sulphurous acid, which interferes with the determination of hydrogen and carbon. The latter cause of error is avoided by placing in the combustion-tube, in front of the oxide of copper, a column of one or two decimetres of oxide of lead, which completely retains the sulphurous acid, (§ 1216.) The quantity of pyrites in the coal may be ascertained by determining, on the one hand, the quantity of sesquioxide of iron which exists in the ashes, and, on the other, the quantity of sulphuric acid yielded by a known weight of coal, powdered very finely, and acted on by fuming nitric acid, or ordinary nitric acid, to which small quantities of chlorate of potassa are gradually added. It is evident that these determinations are necessary only when the combustible produces a large quantity of ashes, and when the latter are very ochrous.

Coal belonging to the secondary and tertiary formations often

yields calcareous ashes, in which case it becomes necessary, before weighing them, to sprinkle them with a solution of carbonate of ammonia, which is subsequently evaporated at a gentle temperature. But the determination of the carbon is generally inaccurate, because the carbonate of lime of the ashes gives off, by contact with the oxide of copper in the combustion-tube, a portion of its carbonic acid; and the oxide of copper must then be replaced by chromate of lead, intimately and largely mixed, with the coal reduced to impalpable powder, (§ 1216,) after which the carbonic acid produced by the carbonates of the ashes, which has been determined by direct weighing of these carbonates, is subtracted from the carbonic acid formed by combustion.

Coal also retains one or two per cent. of hygrometric water, which must be previously driven off by drying it in a stove at  $270^{\circ}$  or  $280^{\circ}$ .

§ 1317. It is necessary, in order to form a correct judgment of the nature of a combustible, to determine the weight of coke it yields by burning; and it is indispensable that this operation should always be conducted under the same circumstances, as the quantity and nature of the coke depend on the manner of calcination. The best method consists in placing 3 gm. of the coal in a thin platinum crucible, accurately covered by its lid, and rapidly heating it to a red-heat. The crucible is kept at a red-heat for eight minutes, and after cooling without being uncovered, the coke is weighed, and carefully examined.\*

§ 1318. The calorific power of fuel is calculated from its chemical composition; admitting that this power is equal to the sum of that of the carbon it contains, and that of the hydrogen obtained by subtracting from the total quantity of hydrogen that which would form water with the oxygen contained in the fuel. This hypothesis is not strictly true, but it may be admitted when the quantities of heat afforded by various kinds of fuel are only to be compared by approximation.†

This comparison is generally made in another way, based on the supposition that the calorific powers of combustibles are in proportion to their reducing powers; that is, to the weight of the same oxide which they can reduce to the metallic state. An intimate mixture of 1 gramme of finely powdered combustible and 40 gm. of litharge being introduced into an earthen crucible, 20 gm. of litharge are added, and the crucible is covered with its lid and rapidly heated to a red-heat. It is allowed to cool, and, after being broken, the lump of lead is weighed, which rapidly separates from the scoria of the litharge; and it is assumed that the calorific powers of combus-

\* Rapid coking is very wasteful of coke, and yields a larger amount of tar and gaseous products.—*J. C. B.*

† M. Bull's experiments on fuel, the best ever made, have shown the fallacy of the assumption named in the text.—*J. C. B.*

tibles are in proportion to the weight of lead yielded by this experiment. This supposition is not absolutely exact, because combustibles yield, before attaining the temperature at which they act on the litharge, a small quantity of volatile substances possessing a reducing power—which substances are more abundant in combustibles of recent formation than in those containing a larger proportion of oxygen.

§ 1319. The following table exhibits the composition of a large number of kinds of mineral fuel, taken from various geological formations, and from the kinds best marked and most extensively applied in the arts. The fragments containing least ashes have also been chosen, in order to cast no uncertainty on the composition of the combustible itself.

The table contains, 1st, the actual composition of the coal, as afforded by direct analysis; and, 2dly, the composition calculated by abstracting the ashes contained:—



TRANSITION ROCKS.	Species of Combustible.	Locality.	Nature of the Coke, and other remarks.
	I. Anthracites.	Pennsylvania.	{ Is found in an argillaceous transition schist; fracture vitreous; coke pulverulent.....
		Wales.....	{ In the lower portion of the coal formation; fracture vitreous and conchoidal; coke pulverulent.....
		Mayenne.....	{ In argillaceous transition schist; fracture conchoidal and vitreous; coke not adherent.....
		Rolduc.....	{ Lower part of the coal formation; fracture vitreous, but texture laminated; coke slightly adherent.....
	II. Fat and hard pit-coal.	Alais (Roche-Belle) .....	{ Coal sandstone; fracture unequal; coke metalloid; slightly swollen or bloated.....
		Rive-de-Gier (P. Henri)..	{ Coal sandstone; fracture schistose; coke metalloid and swollen.....
	III. Fat black-smith's coal.	Rive-de-Gier. 1.	{ Coal formation; of a beautifully black, greasy lustre; very swollen metalloid coke.....
		Rive-de-Gier. 2.	{ Coal formation; of a beautiful black; fracture more schistose; coke rather less swollen.....
		Newcastle....	{ Coal formation; of a beautiful black; fracture schistose and prismatic; coke swollen.....
	IV. Fat pit-coal burning with a long flame.	Flênu of Mons 1.	{ Coal formation; rhomboidal fragments; coke swollen.....
		Idem 2.....	{ Coal formation; less marked rhomboidal cleavage; coke swollen.....
		Rive-de-Gier (cemetery) 1.	{ Coal formation; lustre feeble, texture schistose; coke swollen, but less brilliant.....
		Idem 2.....	{ The same as No. 1.....
		Rive-de-Gier. Couzon 1....	{ Coal formation; lustre more marked, texture very schistose; coke swollen, but less brilliant.....
		Idem 2.....	{ Coal formation; lustre very feeble; fracture unequal, and not schistose; coke less swollen.....
		Lavaysse.....	{ Coal formation; lustre brilliant; fracture conchoidal; coke swollen and light.....
		Lancashire....	{ Coal formation; English <i>cannel-coal</i> ; without lustre; fracture conchoidal; coke fritted and brilliant.....
		Epinae.....	{ Coal formation; lustre brilliant, texture schistose; adherent metalloid coke, but slightly swollen.....
	V. Dry pit-coal burning with a long flame.	Commentry...	{ Coal formation; resembling <i>cannel-coal</i> ; fracture conchoidal; metalloid fritted coke.....
		Blanzy.....	{ Coal formation; fracture laminated; lustre brilliant; coke slightly adherent, but not swollen.....

Density.	Coke yielded by calci- nation.	ELEMENTARY COMPOSITION.				COMPOSITION, THE ASHES BEING REMOVED.		
		Carbon.	Hydrogen.	Oxygen and Nitrogen.	Ashes.	Carbon.	Hydrogen.	Oxygen and Nitrogen.
1.462	89.5	89.21	2.43	3.69	4.67	93.59	2.55	3.86
1.348	91.3	91.29	3.33	4.80	1.58	92.76	3.38	3.86
1.367	90.9	90.72	3.92	4.42	0.94	91.58	3.96	4.46
1.343	89.1	90.20	4.18	3.37	2.25	92.28	4.28	3.44
1.322	77.7	88.05	4.85	5.69	1.41	89.31	4.92	5.77
1.315	76.3	86.65	4.99	5.49	2.96	89.29	5.05	5.66
1.298	68.5	86.25	5.14	6.83	1.78	87.82	5.23	6.95
1.302	69.8	86.59	4.86	7.11	1.44	87.85	4.93	7.22
1.280	"	86.75	5.24	6.61	1.40	87.97	5.31	6.72
1.276	69.8	83.51	5.29	9.10	2.10	85.30	5.40	9.30
1.292	"	82.72	5.42	8.18	3.68	85.88	5.63	8.49
1.288	70.9	80.92	5.27	10.24	3.57	83.91	5.46	10.63
1.294	69.1	83.67	5.61	7.73	2.99	86.25	5.77	7.98
1.298	64.6	81.45	5.59	10.24	2.72	83.73	5.75	10.52
1.311	65.6	80.59	4.99	9.10	5.32	85.12	5.27	9.61
1.284	57.9	81.00	5.27	8.60	5.13	85.38	5.56	9.06
1.317	57.9	82.60	5.66	9.19	2.55	84.63	5.85	9.52
1.353	62.5	80.01	5.10	12.36	2.53	82.08	5.23	12.69
1.319	63.4	81.59	5.29	12.88	0.24	81.79	5.30	12.91
1.362	57.0	75.43	5.23	17.06	2.28	77.19	5.35	17.46

SECONDARY ROCKS.	Species of Combustible.	Locality.	Nature of the Coke, and other remarks.
Inferior stratum.	Anthracites.....	Lamure.....	{ Jurassic formation; grayish-black; lustre vitreous; fracture conchoidal; coke pulverulent.....
	"	Macot.....	{ Jurassic formation; grayish-black; lustre vitreous; coke pulverulent..
Superior stratum.	Pit-coal.....	Obernkirchen	{ Jurassic formation; aspect of fat coals; coke metalloid and swollen.
	"	Ceral.....	{ Marls of the lower oolite; aspect of coals burning with a long flame; coke metalloid and fritted.....
	"	Noroy.....	{ Variegated marls; of a dull black; fracture unequal; coke not adherent.....
	Jet.....	Saint-Girons..	{ Green sandstone; very brilliant; fracture conchoidal; adherent metalloid coke.....
	"	Belestat.....	{ The same as that from Saint Girons.
TERTIARY ROCKS.	I. Perfect lignites.....	Dax.....	{ Of a beautiful black; fracture unequal; free from ligneous texture; coke not adherent.....
		Bouches-du-Rhone.....	{ Schistose; pure and brilliant black; free from ligneous texture; coke not adherent.....
		Mt. Meissner.	{ Brilliant; fracture conchoidal; coke feebly adherent.....
		Lower Alps...	{ Black; lustre greasy; coke slightly swollen.....
	II. Imperfect lignites.....	Greece.....	{ Laminated; of a dull black; indices of vegetable organization; coke not adherent.....
		Cologne.....	{ Umber-coloured; friable; streak reddish-brown; texture ligneous; coke not adherent.....
		Usnach.....	{ Fossil wood; woody texture; very hard.....
	III. Lignites { passing into bitumen.....	Ellebogen.....	{ Compact, homogeneous; fracture conchoidal; very light metalloid coke
		Cuba.....	{ Velvet-black colour; lustre greasy; coke swollen and very light.....
	IV. Asphaltum..	Mexico.....	{ Black; very brilliant; strong smell; melts below 212°; coke exceedingly swollen.....
ALLUVIAL FORMATION.	Turfs or Peats {	Vulcaire.....	{ In a very advanced stage of alteration, though still exhibiting some remains of vegetables.....
		Long.....	{ Similar to the foregoing.....
		Champ-du-Feu.....	{ In a less advanced stage of alteration, though still containing some vegetables.....
	Wood.....	.....	Average composition.....

Density.	Coke yielded by calcination.	ELEMENTARY COMPOSITION.				COMPOSITION, THE ASHES BEING REMOVED.		
		Carbon.	Hydrogen.	Oxygen and Nitrogen.	Ashes.	Carbon.	Hydrogen.	Oxygen and Nitrogen.
1.362	89.5	88.54	1.67	5.22	4.57	92.78	1.75	5.47
1.919	88.9	70.51	0.92	2.10	26.47	95.90	1.25	2.85
1.279	77.8	88.27	4.83	5.90	1.00	89.16	4.88	5.96
1.294	53.3	74.35	4.74	10.05	11.86	83.40	5.32	11.28
1.410	51.2	62.41	4.35	14.04	19.20	77.25	5.38	17.57
1.316	42.5	71.94	5.45	18.53	4.08	75.02	5.69	19.29
1.305	42.0	74.38	5.79	18.94	0.89	75.06	5.84	19.10
1.272	49.1	69.52	5.59	19.90	4.99	73.18	5.88	21.14
1.254	41.1	63.01	4.58	18.98	13.43	72.78	5.29	21.93
1.351	48.5	70.73	4.85	22.65	1.77	72.00	4.93	23.07
1.276	49.5	69.05	5.20	22.74	3.01	71.20	5.36	23.44
1.185	38.9	60.36	5.00	25.62	9.02	66.36	5.49	28.15
1.100	36.1	63.42	4.98	27.11	5.49	66.04	5.27	28.69
1.167	"	55.27	5.70	36.84	2.19	56.50	5.83	37.67
1.157	27.4	72.78	7.46	14.80	4.96	76.58	7.85	15.57
1.197	39.0	74.82	7.25	13.99	3.94	77.88	7.55	14.57
1.063	9.0	78.10	9.30	9.80	2.80	80.34	9.57	10.09
"	"	56.25	5.63	32.54	5.58	59.67	5.96	34.47
"	"	57.29	5.93	32.17	4.61	60.06	6.21	33.73
"	"	57.00	6.11	31.56	5.33	60.21	6.45	33.34
"	"	49.60	5.80	42.56	2.04	50.62	5.94	43.44

§ 1320. In order to see how the composition of mineral combustibles varies with their qualities in the arts and geological age, the numbers contained in the last three columns of the table must be compared; that is, those which exhibit the composition of these combustibles after the ashes are removed. On assuming as a standard of comparison the coals of the third class, and ascending from this to those of the second, it will be found that the quantity of hydrogen is nearly the same, but that the oxygen has remarkably decreased and been replaced by carbon. On passing from the second class to the first, it will be observed that both the hydrogen and oxygen decrease, while the carbon increases in the same ratio.

Starting always from the *blacksmith's coal*, we descend toward the fourth class, and remark that, generally, the hydrogen exists in greater quantity; and that the carbon decreases remarkably and is replaced by oxygen. Lastly, in the fifth class, the oxygen has still increased, and taken the place of a corresponding quantity of carbon.

Fat pit-coal may become dry in two ways: either by passing into anthracite, the hydrogen and oxygen both decreasing, and the carbon increasing in the same ratio, or by approaching the more modern combustibles, the *lignites*, the carbon decreasing and being replaced by oxygen; in which latter case the ratio between the oxygen and hydrogen increases.

By now comparing the combustibles of the secondary with those of the coal formation, it will be seen that, in the inferior stratum of the latter formation, the same variety can be distinguished. Thus, the anthracites of Lamure and Macot, which are found in the lower part of the jurassic rocks, present the same composition as those in the transition rocks; while the coal from Obernkirchen, which also exists in the jurassic formation, has the same properties and composition as those of the carboniferous formation. Lastly, the coal from Céral, which also occurs in the jurassic formation, belongs, on account of its composition and applications in the arts, to the class of fat coal burning with a long flame.

The coal found in the upper stratum of secondary rocks resembles, on the contrary, the combustibles of the tertiary rocks or the lignites, which differ from the coal of the older rocks by containing less carbon and more oxygen; and, as their formation approaches a modern period, their composition resembles more closely that of wood. The charcoal they yield by calcination becomes more and more dry: thus, the jet of chalk still yields a fritted metalloïd coke, while the lignites of the tertiary rocks produce a non-metalloïd charcoal, the fragments of which do not adhere to each other, and resemble in appearance wood charcoal.

The bitumens, which are evidently products of distillation of older combustibles, or produced by the spontaneous decomposition

of animal substances, differ essentially from coal properly so called, by containing much larger quantities of hydrogen.

## ALCOHOLIC FERMENTATION

§ 1321. The majority of vegetables containing amylaceous matter contain, at the same time, substances which can, under favourable circumstances, convert this matter into sugar. These substances are sometimes developed only at certain stages of vegetation; as, *e. g.* the grains of the cerealia contain at the moment of germination a peculiar substance, diastase, (§ 1305,) which chiefly resides at the point of insertion of the germ in the grain, and which, under favourable conditions, rapidly converts starch into a soluble substance, dextrin, and then into sugar, if its action be continued for a sufficient length of time. In these successive transformations the chemical composition of the amylaceous matter is unchanged, while it has become soluble, and may be carried into the circulation of the sap, where it aids in the development of the vegetable, by forming the cellulose which is to constitute the skeleton of the new plant.

Ripe fruits which contain a large quantity of sugar, likewise contain a peculiar substance, called *ferment*, which, under certain circumstances, possesses the property of decomposing the sugary matter into alcohol and carbonic acid; a certain temperature and the contact of oxygen or atmospheric air being required for the exercise of the action. If ripe grapes be expressed under mercury, and the juice collected in a bell-glass completely filled with mercury, it will remain unchanged for several days; but if a few bubbles of oxygen or atmospheric air be introduced into the bell-glass, a considerable volume of gas is disengaged, the evolution of which ceases generally in 2 or 3 days. If the juice be then examined, a volatile liquid, called *alcohol*, will be found to have taken the place of all the sugar; but if the sugary substance of the fruit is not decomposed in the uninjured fruit, it is because the active principle, or ferment, or the substances which produce it, did not come in contact with oxygen, a condition indispensable for the production of fermentation.

Ferment is also produced when animal or vegetable matter is allowed to decompose spontaneously, as in the manufacture of beer, when it is called *yeast of beer*, or simply *yeast*, which substance soon effects the fermentation of the aqueous solution of the sugars and their complete conversion into alcohol and carbonic acid. Muscular flesh, urine, gelatin, white of eggs, cheese, gluten, legumin, extracts of meat and blood, left to themselves for some time, exposed to air and moisture, and thus undergoing the process known as putrefaction, cause sugars to ferment, and convert them into alcohol and carbonic acid.

All the sugars above described undergo this decomposition under the influence of ferment, and it is a distinctive character of this

class of organic products, although they do not all experience it in the same space of time; the sugar of acid fruits turning to the left, the solid sugar of dry fruits and glucose being very rapidly destroyed by fermentation, while cane-sugar requires a longer time. It is even easy to perceive, by the inversion of the rotatory powers, that cane-sugar undergoes fermentation only after being converted into fruit-sugar. Fresh ferment always contains a considerable quantity of acid, which first changes the cane-sugar into fruit sugar; but as vegetable acids require considerable time to effect this transformation, its fermentation is very slow. Yeast, freed from these acids by washing, for a long time exerts no action on cane-sugar, and fermentation commences only when fresh quantities of acid are formed by the spontaneous change in the yeast from exposure to air and water. If, on the contrary, the acid liquid arising from washing the yeast be added to the solution of sugar, the cane-sugar is gradually transformed into fruit-sugar, which immediately ferments when brought into contact with the washed yeast.

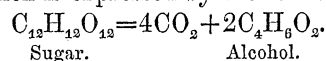
One hundred parts of fruit-sugar yield by fermentation

48.88 of carbonic acid

and

51.12 of alcohol;

so that the chemical elements of the yeast appear to have no agency in the reaction, which is expressed by the following equation:



§ 1322. That the decomposition of sugar by fermentation is effected only by the immediate contact of yeast, is easily shown by the following experiment:—Having adapted, by means of a cork, to the mouth of a bottle A, (fig. 666,) containing a solution of sugar, a large tube *ab* open at both ends, the lower one of which is covered by a sheet of bibulous paper, a small quantity of yeast of beer slightly diluted with water is introduced into the tube. As the solution of sugar penetrates the tube *ab* through the paper, fermentation ensues very actively, and carbonic acid is copiously disengaged, while no similar reaction takes place in the liquor in the bottle, which remains unchanged for any length of time.

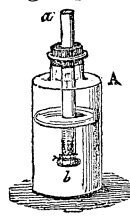


Fig. 666.

During the decomposition of sugar by fermentation, the ferment itself is destroyed, so that a small quantity of the active principle cannot decompose an indefinite quantity of sugar; and if the proportion of yeast be too small, its decomposition is effected before that of the sugar, a portion of which then remains unchanged in the liquor. If, on the contrary, the yeast predominates, the decomposition of the sugar is effected before that of the yeast, and the latter continues to change spontaneously; and if an additional quantity of the solution of sugar be introduced, it produces fermentation until it is entirely destroyed. The best proportions to induce

rapid fermentation are 1 part of cane-sugar, 3 or 4 of water, and  $\frac{1}{4}$  of fresh yeast; and if the proportion of sugar be increased, the fermentation becomes less active, and ceases entirely if a saturated solution of sugar be used. In all cases sugar does not destroy more than 2 per cent. of its weight of ferment.

The weak acids, in small quantities, increase fermentation, while alkalies, on the contrary, arrest or completely modify the process.

§ 1323. Ferment is a species of microscopic vegetable, which is spontaneously developed in the organs of plants, and in a large number of nitrogenous substances when left to putrefy; and which is also formed by exposing to the ordinary temperature a solution of sugar mixed with albuminous substances of vegetable or animal origin. After some time the liquor becomes cloudy, and small ovoidal bodies are deposited, gradually increasing in size until they attain a diameter of the  $\frac{1}{100}$  of a millimetre. Two species of ferments, differing in their manner of development and mode of action on solutions of sugar, may be observed. The first, called *upper yeast*, is developed in a mixture of sugar and water and albuminous substances, when the temperature is comprised between  $64.5^{\circ}$  and  $77^{\circ}$ ; while the second, or *lower yeast*, is only found at temperatures between  $32^{\circ}$  and  $46.4^{\circ}$ . In order to study the shape and development of the globules under the microscope, a very small quantity of yeast is diluted in an infusion of grain, sprouted barley for example, and a drop of the liquid is placed between two pieces of thin glass, the edges of which are luted to prevent the evaporation of the water. These plates are placed under the microscope, taking care to bring an isolated globule of yeast under the centre cross-threads of the micrometer, in order to study its development. Figs. 667 to 674 represent the arrangement of the new globules of ferment which form successively around an original globule 1, the temperature being about  $66.2^{\circ}$ . During the first two hours the globule 1 (fig. 667) exhibits nothing peculiar; while, after this period, there forms at a point of its surface a rupture which gradually increases for six hours, until it has attained the dimensions of the original globule, (fig. 668.) The second globule soon generates a third, which arises on the sides of the second (figs. 669 and 670) in the same way as this grew on the first, and so on. In an experiment lasting three days, 30 globules (fig. 674) had formed around the original globule 1; and on the fourth day another formed, which was the last, the albuminous matter necessary for their formation having probably been exhausted. Six successive generations, which were thus observed, are indicated in the figures by ciphers, according to the order of their origin. The various globules adhered to each other, but there appeared to be no intercommunication.

It will hence be perceived that, on adding an albuminous substance to a mixture of sugar and ferment, the sugar is not alone



affected by the ferment, as the albuminous matter itself undergoes several metamorphoses and is converted into yeast; which fact explains the reason why, in breweries, at the close of the operation,



Fig. 667.



Fig. 668.



Fig. 669.

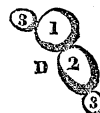


Fig. 670.

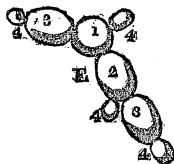


Fig. 671.

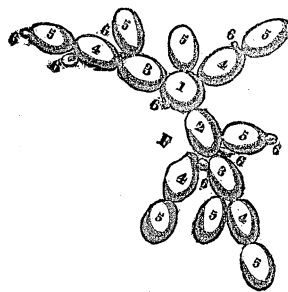


Fig. 672.

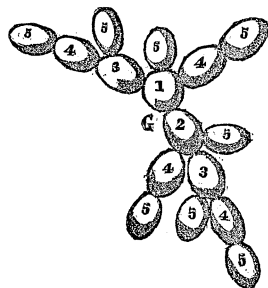


Fig. 673.

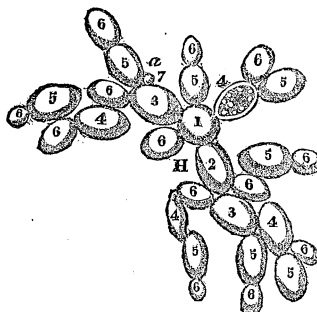


Fig. 674.

a quantity of yeast is withdrawn seven or eight times greater than that which had been originally used. The yeast is carefully collected, and subsequently used to effect other fermentations, particularly in the making of bread.

It is easy to observe that each globule is composed of a solid envelope containing a liquid; and it therefore forms a sort of cell, which is lined with a layer of mucilaginous substance. On observing for several days the systems of globules which have acquired their perfect development, it will be seen that smaller granules, whose rapid motion proves that they float in a liquid, are formed in each globule; and after a sufficient length of time the whole of the contained liquid is converted into granules.

The globules the development of which we have followed belong

to the upper yeast; and it is easy to see that they are formed by *shoots* upon each other. The lower yeast is always composed of isolated globules scattered through the liquid; their formation obeying the same laws as those of the upper yeast, while the temperature must not exceed  $44.6^{\circ}$  or  $46.4^{\circ}$ . Each globule appears at first like an isolated point in the liquid, and gradually increases until it attains a diameter of about  $\frac{1}{100}$  of a millimetre. Some observers think that the old globules of lower yeast burst and suspend in the liquor the granules they contain, each of which would then be transformed into a globule; in which case the mode of generation of the lower would differ totally from that of the upper yeast. If the temperature be raised to  $68^{\circ}$  or  $77^{\circ}$ , the isolated globules of lower yeast are immediately developed by shoots, and then produce upper yeast.

§ 1324. The action of the two kinds of yeast on solutions of sugar is also very different; upper yeast producing a much more active fermentation, with a copious evolution of carbonic acid, while the yeast is violently agitated in the liquid, and ascends to its surface; while, on the other hand, lower yeast acts much more slowly, and frequently requires two or three months to effect the complete transformation of sugar into alcohol and carbonic acid, the ferment being disturbed by no rapid movement, but on the contrary gently deposited at the bottom of the liquid. Lower yeast is used in the manufacture of certain kinds of beer, particularly that called Bavarian.

It has been impossible to follow with the microscope the transformations of yeast during the fermentation of sugar, on account of the disengagement of carbonic acid; and it has been merely ascertained that the yeast increases by about  $\frac{1}{4}$  of its weight. Its chemical composition is also changed; and while fresh yeast has been found to contain

Carbon .....	47.0
Hydrogen.....	6.6
Nitrogen.....	10.0
Oxygen, about .....	35.0

and, in addition, small quantities of sulphur, phosphorus, and some mineral bases, such as potassa and lime; the same yeast, after fermentation was composed of

Carbon .....	47.6
Hydrogen.....	7.2
Nitrogen.....	5.0

Thus, the carbon remained nearly the same, while the hydrogen sensibly increased, and the nitrogen decreased by one-half.

On bringing an aqueous solution of iodine into contact with globules of ferment, the outer envelope is not coloured, while the

liquid inside becomes of a brown colour, which may be proved by crushing the globules between plates of glass, when the envelopes exhibit the characters of cellulose. When a certain quantity of yeast is allowed to decompose completely, in contact with a solution of sugar, and the residue is bruised in a mortar, and perfectly exhausted by water, alcohol, and ether, a white substance remains, which yields glucose with sulphuric acid, and does not dissolve in alkaline liquids, which, on the contrary, immediately dissolve the albuminous substances in yeast.\*

§ 1325. Ferment, dried in vacuo or at a low temperature, yields a hard, corneous, semi-transparent, and reddish-gray mass; the property of which, of causing the fermentation of saccharine liquors, is only suspended, and is again called forth by digesting the substance for some time in water. If it be boiled for a few moments, it loses this property; but may recover it by contact with the air, when it has not been exposed for too long a period to a temperature of  $212^{\circ}$ . Alcohol, sea-salt, and a great excess of sugar, oxide of mercury, corrosive sublimate, pyroligneous acid, sulphurous acid, nitrate of silver, the essential oils, etc. etc. destroy the fermenting power of yeast; while certain substances, which are very violent poisons to animals, such as arsenious acid and tartar emetic, do not produce this effect; and neither do these substances prevent the fermentation of certain microscopic plants, for solutions of tartar emetic, if exposed to the air, become covered with *confervæ*.

The action by which ferment converts sugar into alcohol and carbonic acid is yet unexplained. Some chemists insist that vital force causes the development and successive metamorphoses of the globules of ferment; while others think that ferment only acts by its presence, and that its action should be compared to that by which certain mineral substances effect the decomposition of feeble compounds without any change in their elementary composition. Thus, binoxide of manganese will decompose binoxide of hydrogen into oxygen and water, without being itself in the least changed; and so again, chlorate of potassa, which is decomposed only at a temperature of  $930^{\circ}$  or  $1020^{\circ}$  when heated alone, experiences this decomposition at a much lower temperature when it is intimately mixed with oxide of copper or binoxide of manganese, oxides which remain unchanged in the residue. Lastly, according to some authors, the movements of the particles of ferment during their successive metamorphoses are the principal cause of the decomposition of sugar; as these movements, by being communicated to the saccharine par-

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\* In an investigation of the products of the spontaneous decomposition, or fermentation, of yeast of beer alone, I found the liquid contained in the small cells to be completely decomposed into butyric acid with traces of valerianic, and into a substance the behaviour of which corresponded in all respects to leucin, but the analysis of which was unfortunately prevented by accident.—*W. L. F.*

ticles, destroy their inertia, and cause the elementary molecules to be grouped so as to form more fixed compounds. We shall be satisfied with stating what is known concerning alcoholic fermentation, and shall venture no explanation of this mysterious phenomenon, which is as yet too imperfectly understood to allow the establishment of any theory upon certain data.

*Alcohol*  $C_4H_6O_2$ .

§1326. It has been mentioned that a solution of sugar, when left for some time in contact with yeast of beer, soon ferments, and is converted into alcohol and carbonic acid; but the same decomposition takes place spontaneously in the saccharine juice of many fruits, such as grapes, cherries, currants, apples, pears, etc.; and also ensues, when assisted by yeast, in the saccharine liquors produced by amylaceous substances in the presence of diastase. The alcohol remains in the liquor, and may be separated from it by distillation, because it is more volatile than water. In fact, on distilling in an alembic, wine, beer, cider, or other alcoholic liquors, the first portions of liquid which pass over are much richer in alcohol than the residue; and if the distillation be arrested at the proper moment, the residue contains scarcely any alcohol. For this purpose, alcoholic liquors are used, the production of which exceeds their consumption, or the inferior quality of which renders them unfit for market.

If the distilled portions be redistilled, the first liquors are still richer in alcohol, and thus alcoholic liquors are obtained bearing different names, according to their strength; and while liquors containing 50 to 55 per cent. of alcohol are called *brandies*, those containing more are called *spirits*. By a proper process of distillation, liquors containing from 85 to 90 per cent. of alcohol may be obtained, which then nearly consist of

1 eq. of alcohol $C_4H_6O_2$ .....	46 .....	83.7
1 eq. of water.....	9 .....	16.3
	<hr/>	
	55 .....	100.0

The last portions of water cannot be removed by distillation, but they are separated by combining them with substances which have a great affinity for water, and which do not unite permanently with alcohol.

The best method of obtaining anhydrous alcohol consists in pouring alcohol of 85 or 90 per cent. into a large bottle containing quicklime prepared by the process mentioned § 555, shaking the bottle several times, and allowing it to rest for 24 hours; after which the liquid is distilled in a water-bath, arranged as in fig. 149, until no more liquid passes over. The alcohol thus obtained being not entirely freed from water, the operation must be renewed; but this process will often not yield completely anhydrous alcohol; and

the highly concentrated alcohol must be dissolved in a certain quantity of melted caustic potassa, and distilled over a fire, or in a bath of chloride of calcium, until  $\frac{3}{4}$  of the liquor have passed over. The distilled liquid, which is then anhydrous or *absolute alcohol*, has a peculiar odour, owing probably to the presence of a small quantity of volatile oil, formed by the reaction of the oxygen of the air on the alcohol in the presence of alkaline substances. The alcoholic liquor which remains in the distilling apparatus is coloured brown by a small quantity of resinous matter, also produced by the reaction.

§ 1327. Absolute alcohol is a colourless liquid, more fluid than water, of a burning taste and agreeable odour. It does not solidify, even at the lowest temperature which can be produced; and it boils at the temperature of  $173.1^{\circ}$  under a pressure of 760 millimetres, or 29.92 inches. The density of its vapour, compared with air, is 1.5890; and its specific gravity in the fluid state is,

At $32^{\circ}$ .....	0.8151	At $59^{\circ}$ .....	0.8021
41 .....	0.8108	68 .....	0.7978
50 .....	0.8065	77 .....	0.7933

Alcohol is composed of

4 eq. of carbon.....	24	.....	52.65
6 eq. of hydrogen.....	6	.....	12.90
2 eq. of oxygen.....	16	.....	34.45
	46		100.00

1 volume of vapour of alcohol contains

1 vol. of vapour of carbon.....	0.8290
1 “ “ hydrogen.....	0.2074
$\frac{1}{2}$ “ “ oxygen .....	0.5526
	1.5890

Its equivalent  $C_4H_6O_2$  is therefore represented by 4 volumes of vapour, (§ 1237.)

A weak solution of alcohol, left in a bladder exposed to the air, allows more water than alcohol to pass, and in time becomes stronger.

Absolute alcohol attracts the moisture of the air. The temperature rises and contraction ensues when it is mixed with water; the maximum of contraction being produced by mixing

53.7 volumes of alcohol,
49.8 “ water,
103.5

which are reduced to 100 volumes; which proportions correspond to 1 equivalent of alcohol and 6 equivalents of water. Very cold absolute alcohol, mixed with snow, lowers the temperature to  $34.6^{\circ}$ ; all which facts show a powerful affinity between alcohol and water:

the two liquids, however, dissolve each other, in all proportions. Alcohol burns in the air with a feebly brilliant flame, and in the open air its combustion is perfect.

Alcohol is frequently used, either absolute, or mixed with greater or less proportions of water, in the laboratory as a solvent. Generally speaking, it dissolves gases more largely than water; and a great number of very soluble and deliquescent compounds dissolve in even absolute alcohol, as, for example, caustic potassa and soda, the chlorides of calcium, strontium, nitrates of lime, magnesia, etc. etc.; and it frequently dissolves certain compounds which are not very soluble in water more freely than the latter liquid, as, for example, corrosive sublimate, and the corresponding bromide and iodide of mercury. Lastly, it dissolves a large number of organic substances insoluble in water. Alcohol is frequently used in chemical analyses, in order to separate substances soluble in water but very unequally soluble in alcohol; the differences of solubility being sometimes increased by adding ether to the alcohol.

Alcohol also combines with several salts, which are soluble in it, playing a part analogous to that of water of crystallization, and forming compounds, called *alcoates*. When dry chloride of calcium is brought into contact with alcohol, the temperature rises considerably, in consequence of the formation of an alcoate.

When substances are dissolved in alcohol, their reactions are frequently very different from those of their solutions in water. It has been mentioned (§ 378) that acetic acid will readily expel carbonic acid from carbonate of potassa dissolved in water; but, on the other hand, carbonic acid will displace the acetic acid of acetate of potassa dissolved in alcohol; the insolubility of carbonate of potassa in alcohol thus becoming a new condition, which changes the order of affinities.

§ 1328. By adding larger and larger proportions of water to alcohol, its specific gravity increases progressively; and processes for determining the richness in alcohol of these mixtures have been based on the variation of density. An areometer was formerly used, called *Cartier's hydrometer for spirits*, which marked 0° in pure water and 44° in absolute alcohol, the space between these points being divided into 44 equal parts; but this instrument has been superseded by *Gay Lussac's alcoholometer*, of which the graduation marks the richness immediately in hundredths. The zero of the instrument corresponds to pure water, while absolute alcohol marks 100; and several intermediate points have been fixed by plunging it into liquors the composition of which was known. The centesimal alcoholometer only gives the exact quantity of alcohol when the liquid is at a temperature of 59°, at which the graduation was made; and as alcohol expands considerably by heat, corrections must be made for all other temperatures; which have been carefully

calculated and set down in tables for a certain extent of the thermometric scale.

The alcoholometer can show the richness in alcohol only of those liquids which contain merely water and alcohol; for if they contained sugar or saline substances, the result would be inaccurate, because these substances would increase the density of the liquor. This process, therefore, cannot indicate immediately the richness of alcoholic drinks, which always contain sugar and saline substances; and for this purpose the following method is used:—After introducing 300 cub. cent. of the liquor to be tested into a small alembic of tinned copper, it is distilled by means of an alcohol-lamp, and the liquid which condenses in the worm is collected in a test-tube, graduated to cubic centimetres. The distillation is arrested as soon as 100 cub. cent. have collected, when the liquor is reduced to the temperature of  $59^{\circ}$ , and the quantity of alcohol it contains determined by the alcoholometer; after which  $\frac{1}{3}$  of the quantity found represents the richness in alcohol of the liquor subjected to the test.

If the liquor were very poor in alcohol, only 50 cub. cent. would be distilled, in order to obtain a distilled liquor somewhat rich in alcohol, for the test then affords a greater degree of accuracy, and the percentage of alcohol in the liquor tested is, in this case,  $\frac{1}{3}$  of that obtained on the product distilled. If, on the contrary, the liquor were very rich in alcohol, it would be proper to distil only  $\frac{1}{2}$  or  $\frac{2}{3}$  of it, and take the  $\frac{1}{2}$  or  $\frac{2}{3}$  of the standard found.

The richness of an alcoholic liquor may also be determined by ascertaining the temperature marked by a thermometer, the bulb of which is dipped into the liquor at the moment it boils. A table, which shows the temperature of ebullition corresponding to the various mixtures of alcohol and water, must then be made, and deduced from direct experiments made in the same apparatus and on known mixtures of alcohol and water. This process shows the richness of alcoholic liquors used as beverages pretty exactly, because the quantities of sugar and salt they contain affect their temperature of ebullition but slightly.

Lastly, the calculation may be based on the great differences of expansibility between alcohol and water, by using a kind of thermometer having the form of a pipette, the lower tube terminating the bulb of which is very short, and its orifice may be closed by a stopper fitting exactly by means of a spring. The liquor to be tested is brought exactly to the temperature of  $77^{\circ}$ , and the thermometric apparatus, having the lower orifice open, is plunged into it. The fluid is made to rise by means of sucking above the zero in the upper graduated stem; and it is then allowed to recede slowly until it exactly reaches the division 0. The stopper being then fitted, and the apparatus immediately introduced into a vessel containing water at  $122^{\circ}$ , the division at which the level of the liquid remains stationary indicates the richness in alcohol, because the instrument

has been graduated by direct experiments made on mixtures of alcohol and water, the composition of which was exactly known. This process is applicable to alcoholic liquors containing sugar or salts, because they influence but slightly the expansibility of the liquid.

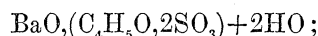
Concentrated alcohol acts as a poison on the animal economy, and will produce death when taken in large quantities; but when more dilute, its effects are merely intoxication. Injected into the veins, it produces almost sudden death, by coagulating the albumen of the blood.

#### PRODUCTS OF THE ACTION OF SULPHURIC ACID ON ALCOHOL.

§ 1329. When brought into contact with sulphuric acid in various proportions and at different temperatures, alcohol yields several very important products, which are now to be described.

##### SULPHOVINIC ACID $C_4H_5O, 2SO_3 + HO$ .

§ 1330. By pouring concentrated sulphuric acid into absolute alcohol, the two liquids dissolve with an elevation of temperature, while a peculiar acid, called *sulphovinic*, is formed, the best proportion for producing which is 1 part of alcohol to 2 parts of sulphuric acid. A considerable quantity of sulphovinic acid is also formed when alcohol of 85 per cent. is substituted for absolute alcohol; but if the alcohol is more dilute, the proportion of sulphovinic acid is very small: the temperature must be prevented, during the reaction, from rising above  $158^\circ$ , for which reason the alcohol should be added very gradually. The liquid is then diluted with water and saturated with carbonate of baryta, with which the excess of sulphuric acid forms the insoluble sulphate, while the sulphovinic acid yields a soluble salt. The liquid being evaporated at a gentle heat, or still better, in vacuo, a salt crystallized in beautiful colourless laminæ is obtained. The formula of crystallized sulphovinate of baryta is



but it readily parts with these two equivalents of water, in a dry vacuum, at a temperature between  $104^\circ$  and  $122^\circ$ .

The sulphovinic acid may be easily extracted from sulphovinate of baryta, by pouring sulphuric acid, drop by drop, into a solution of the salt, until a precipitate is no longer formed; when an acid liquid is obtained, which, being evaporated in a cool place, under the receiver of an air-pump, finally leaves sulphovinic acid in its highest state of concentration, as a syrupy liquid of the formula  $HO, (C_4H_5O, 2SO_3)$ . It decomposes very easily, even at the ordinary temperature, the decomposition becoming very rapid if it is heated, when free sulphuric acid is found in the liquid.

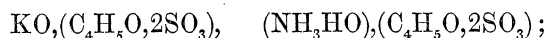
Two equivalents of anhydrous sulphuric acid combine in this re-



action with 1 equivalent of alcohol  $C_4H_6O_2$  and form sulphovinic acid  $C_4H_6O_2, 2SO_3$ ; but the formula of the acid must be written  $HO, (C_4H_5O, 2SO_3)$ , as the equivalent of water may be replaced by 1 equivalent of base. Anhydrous sulphovinates may be regarded as double sulphates of the base and the substance  $C_4H_5O$ , or *ether*, which shall soon be treated of, or an isomeric of this body.

All the sulphovinates being soluble, they are easily made, by double decomposition, by pouring into a solution of sulphovinate of baryta a soluble sulphate of the base, until a precipitate ceases to form. Generally speaking, they crystallize readily.

Crystallized sulphovinates of potassa and ammonia are anhydrous, and their formulæ are



that of crystallized sulphovinate of lime is  $CaO, (C_4H_5O, 2SO_3) + HO$ ; and it loses its water in vacuo. Crystallized sulphovinate of copper is represented by  $CuO, (C_4H_5O, 2SO_3) + 4HO$ , and that of silver by  $AgO, (C_4H_5O, 2SO_3) + 2HO$ .

Solutions of the sulphovinates are easily decomposed by boiling; and the dry salts of the acid yields, when heated, an oleaginous product, which will subsequently be met with under the name of *heavy oil of wine*.

#### ETHER $C_4H_5O$ .

§ 1331. By heating to  $185^\circ$  a mixture of 2 parts of alcohol and 3 parts of concentrated sulphuric acid, a very volatile liquid, called ether, of which the formula is  $C_4H_5O$ , is formed. The formula of alcohol being  $C_4H_6O_2$ , we are naturally led to admit that the alcohol parts with 1 equivalent of water to the sulphuric acid, and is converted into ether  $C_4H_5O$ ; but on examining the reaction more closely, it will not be found quite so simple. In fact, the ether does not pass over alone in distillation, as water distils at the same time, and in such quantity that it would exactly reproduce alcohol with ether formed; for which reason it cannot be admitted that alcohol is transformed into ether by the affinity of sulphuric acid for water.

In order to analyze all the circumstances of the production of ether, the operation must be arranged as follows:—Place in a flask A (fig. 675) 100 parts of concentrated sulphuric acid, containing consequently 18.5 of water, and add 20 parts of water and 50 of absolute alcohol; then close the mouth of the flask with a cork pierced with three holes, through one of which passes a thermometer  $t$ , the bulb of which enters the fluid mixture, while the second is traversed by a tube  $ab$  descending to the bottom of the flask and terminating in a funnel  $a$ ; and lastly, through the third hole passes a curved tube  $cde$ , the end  $e$  of which is drawn out so that the liquid drops which condense in it may fall more easily into the balloon.

The tube *cde* is fitted to an ordinary cooling apparatus BC, resembling that used in distilling, the end *fg* of the cooled tube being bent in order that it may descend to the bottom of the bottle D.

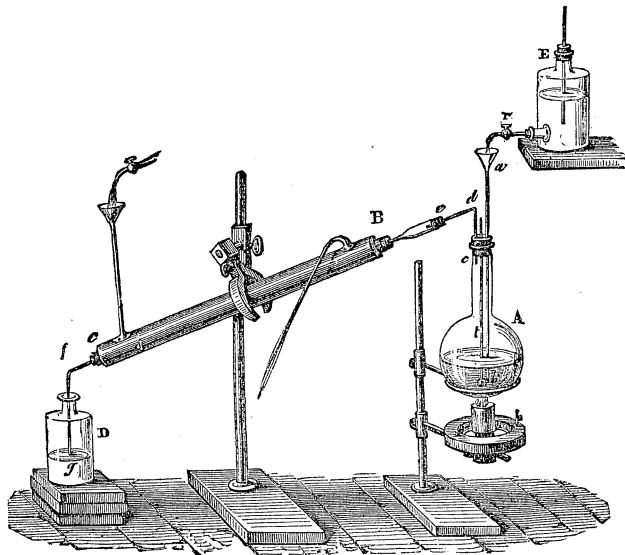


Fig. 675.

The flask is heated with an alcohol-lamp until the thermometer marks  $284^{\circ}$ , while a small circular piece of paper pasted on the balloon indicates the original level of the liquid. After carefully opening the stopcock *r*, in order to allow the flow of a continuous current of absolute alcohol contained in the bottle E, the current is so regulated that the thermometer *t* shall always mark  $284^{\circ}$ ; and if the temperature should rise above this point, more alcohol is poured in; while if, on the contrary, the temperature falls, the stream of alcohol is diminished.

A mixture of ether and water which collects in the bottle D then distils constantly, and care must be taken to keep very cold water in the refrigerator BC. For greater certainty, the tube *fg* is slightly dipped into the bottle D, when a stratum of liquid has collected there; and as the level of the latter rises, the bottle is gradually lowered. By operating in this manner, ether may be formed, with the same quantity of sulphuric acid, from an almost indefinite quantity of alcohol. The bottle D receives a mixture of water and ether, the weight of which is exactly equal to that of the alcohol used, if the flask has been carefully maintained at the temperature of  $284^{\circ}$ , and the ether and water exist in this mixture precisely in the proportions constituting alcohol.

The sulphuric acid, under the circumstances in which the opera-

VOL. II.—2 T

tion has been performed, has merely effected the separation of the alcohol into ether and water, without attacking either of these products; and the affinity of sulphuric acid for water did not therefore cause the reaction. Alcohol may moreover be distilled with a large excess of caustic potassa, or its vapours be passed over potassa heated to any temperature, without ether being formed, and yet potassa has a greater affinity for water than sulphuric acid.

As by the direct mixture of alcohol with sulphuric acid sulphovinic acid is formed, it might be supposed that this acid plays a part in the phenomenon: it might, for example, be assumed that when the alcohol comes into contact with the sulphuric acid, the temperature is depressed by the arrival of cold alcohol sufficiently to allow sulphovinic acid to form, and that this acid, expanding afterward in the heated mixture, is decomposed into ether and sulphuric acid. But it must be remembered that, by placing in the flask A (fig. 675) sulphuric acid diluted with water sufficient to make it boil naturally at  $293^{\circ}$  under the ordinary pressure of the atmosphere, and by passing into the acid vapours of alcohol heated to  $212^{\circ}$  or over, there distils constantly a mixture of ether and water, with a small quantity of alcohol; which arises from the circumstance that a portion of the alcoholic vapours escape the action of the sulphuric acid. It is difficult to admit that sulphovinic acid is formed in this case, for it would be necessary to grant that the acid was formed and decomposed under the same circumstances.

The transformation of alcohol into ether by sulphuric acid is therefore as yet an unexplained phenomenon, unless we admit that sulphuric acid here exerts an action of presence, or catalytic action; which is putting a word in the place of a fact.

A highly concentrated solution of phosphoric acid also converts alcohol when hot into ether and water, but the water is retained by the phosphoric acid; and when it is sufficiently hydrated, it no longer acts on the alcohol. Several chlorides and fluorides, for example the chloride of boron, effect the same transformation, as well as several metallic chlorides. The anhydrous chloride of zinc dissolves largely in alcohol; and if the liquor be distilled, alcohol first passes over; but the temperature now rising above  $392^{\circ}$ , a large quantity of ether, which distils over with the alcohol, is formed; and if the heat be continued, two carburetted hydrogens pass over with the ether; the formula of one, which boils below  $212^{\circ}$ , being  $C_8H_9$ , and the density of its vapour 3.96, while the formula of the second, which boils at about  $572^{\circ}$ , and is of a syrupy consistence, is  $C_8H_7$ . It should be remarked that  $C_8H_9 + C_8H_7 = 4C_4H_6O_2 - 8HO$ ; thus, 4 equiv. of alcohol would yield 1 equiv. of each of these substances, by losing 8 equiv. of water.

Ether is manufactured on a large scale by a continuous process analogous to that just described; the distillation being arrested when the sulphuric acid has transformed into ether a weight of

alcohol 30 or 40 times greater than its own; for if it were continued for a longer time, the ether would be impure and contain a considerable quantity of oil of wine. The ether collected in the receiver is shaken with a small quantity of water, which dissolves the greater portion of the alcohol it contains, after which it is mixed with milk of lime, and distilled after some time in a water-bath. The lime retains the acid products which the ether may contain, while the ether distilled still retains water and alcohol; to free it entirely from which it must be digested with a large quantity of powdered chloride of calcium and distilled by means of a water-bath.

When the alcohol which is to be converted into ether contains a large proportion of water, or when the sulphuric acid is very aqueous, ether is not generated, but water and alcohol pass over. If the alcohol is in excess, it passes over isolated until the residue contains alcohol and sulphuric acid in the proportions which form ether, and then the ordinary transformation into ether and water commences.

By rectifying considerable quantities of crude ether over lime, a yellow oleaginous liquid remains in the distilling vessel, which, being distilled several times over lime and then over potassium, becomes fluid and completely colourless. Its density is 0.897, and it boils at  $545^{\circ}$ . This carburetted hydrogen is probably furnished by the impure alcohol used in the preparation of ether.

§ 1332. Ether is a colourless, very fluid liquid, of an agreeable and pungent odour, and an acid and burning taste. Its density at  $32^{\circ}$  is 0.736, and it boils at  $95.9^{\circ}$  under the pressure of 29.92 inches, the density of its vapour being 2.586. Its composition is expressed by

4 eq. of carbon.....	24	.....	65.31
5 “ hydrogen.....	5	.....	13.33
1 “ oxygen.....	8	.....	21.36
	<u>37</u>		<u>100.00</u>

One vol. of vapour of ether contains

2 vol. of vapour of carbon.....	1.6876
5 “ hydrogen.....	0.3465
$\frac{1}{2}$ “ oxygen.....	0.5528
	<u>2.5869</u>

and its equivalent  $C_4H_5O$  is therefore represented by 2 volumes of vapour.

Ether is very inflammable, and burns with a flame possessing a certain degree of brilliancy, and depositing lamp-black on cold substances introduced into it. Being extremely volatile, it evaporates rapidly in the air, producing detonating mixtures which have occasioned serious accidents.

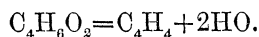
Ether is soon changed by the oxygen of the air, which converts it into acetic acid; and in order to preserve it in a state of purity, it should be kept in well-stoppered bottles, completely filled, or better still, in tubes hermetically closed. The alteration is more rapid under the influence of alkaline bases. Ether dissolves in 9 parts of water; and if a larger quantity of ether be added, the portion which does not dissolve floats on the water. Ether also dissolves a small quantity of water, while alcohol and ether dissolve each other in all proportions.

Ether dissolves about  $\frac{1}{100}$  of sulphur and  $\frac{2}{100}$  of phosphorus, which substances separate in the form of crystals after evaporation. Chlorine and bromine act powerfully on ether, and yield peculiar products, which shall soon be described; while iodine at first simply dissolves in it, but is changed in a short time.

Ether exerts an energetic action on the animal economy: its vapour being rapidly absorbed by the respiratory organs, soon causes a kind of intoxication, accompanied by insensibility, which curious effect has been latterly applied as an anæsthetic agent in surgical operations.

#### BICARBURETTED HYDROGEN, OR OLEFIANT GAS, $C_4H_4$ .

§ 1333. When an excess of concentrated sulphuric acid acts upon alcohol at a temperature of  $320^\circ$  or over, only a small quantity of ether results, while a gaseous carburetted hydrogen of the formula  $C_4H_4$  is formed. On comparing the formula of this body with that of alcohol, it would be natural to explain the decomposition by assuming that sulphuric acid determines the formation of 2 equiv. of water, which combine with it, and that it sets free bicarburetted hydrogen  $C_4H_4$ .



But the following experiment seems to contradict this explanation, Having placed in the flask A (fig. 676) concentrated sulphuric acid,

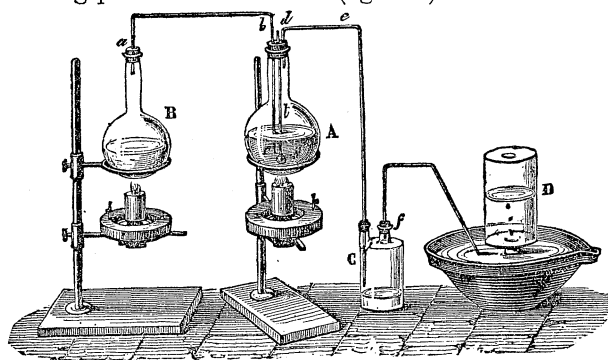


Fig. 676.

to which a quantity of water has been added, such that the mixture shall boil at about  $320^\circ$ , (for which purpose 100 parts of monohydrated sulphuric acid

and 30 of water must be used,) the acid is heated to boiling. The flask B contains absolute alcohol, which is heated to ebullition, and the vapours of alcohol traverse the flask A, the temperature of which is kept constantly at about  $329^{\circ}$ , by allowing more or less alcohol to enter, and by increasing or diminishing the flame of the lamp which heats the flask. Olefiant gas is disengaged in the form of small bubbles from the acid mixture, and carries over vapours of water and alcohol, which condense in the bottle C, while the gas may be collected in a gasometer, or in bottle D over a pneumatic trough. The alcohol carried over is that which has escaped the action of the sulphuric acid, and the water which distils is exactly equal to that which would form alcohol with the bicarburetted hydrogen; while the acid liquor in the flask A retains the same composition, and can convert an almost indefinite quantity of alcohol into bicarburetted hydrogen and water; very little ether being formed. The experiment shows that the decomposition of alcohol into bicarburetted hydrogen and water, by contact with sulphuric acid, is not owing to the affinity of the acid for water, since water and olefiant gas are both disengaged at the same time.

Bicarburetted hydrogen is generally prepared in the laboratory by heating a mixture of 1 part of alcohol at 0.85 and 6 parts of concentrated sulphuric acid in a retort, (fig. 285,) which should be only be  $\frac{1}{3}$  filled; the gas evolved being made to pass first through a bottle containing concentrated sulphuric acid, which retains the vapours of alcohol and ether, and then through a second bottle containing a solution of caustic potassa, to absorb the sulphurous acid and carbonic acid which are copiously evolved toward the close of the operation; the cause of which evolution is the reaction which ensues between the concentrated sulphuric acid and the carbonaceous substances remaining in the retort. The disengagement of gas, which is pretty regular at the commencement of the operation, soon becomes tumultuous and violent, when the acid mixture turns black, becomes viscous, and swells to such a degree that if the retort be not very large it will fill the neck. At the end of the experiment there remains in the retort a solid black substance, which gives off to water sulphuric acid, and sulphovinic acid, or an isomeric of it; while the composition of the black insoluble residue is very complex, and corresponds to the formula  $C_{80}H_{24}O_{20}S_3$ .

§ 1334. Bicarburetted hydrogen is a colourless gas which does not liquefy at the lowest temperatures: its density is 0.978, and it burns with a very brilliant flame, which deposits a large quantity of lamp-black on cold substances immersed in it. When passed through a porcelain tube heated to redness, charcoal is deposited on the sides of the tube, and it is transformed into protocarburetted hydrogen; but if the temperature is more elevated, all the carbon is deposited, and hydrogen only disengaged. The formula of bicarburetted hy-

drogen is  $C_4H_4$ , (266,) and its equivalent is represented by 4 volumes of gas.

§ 1335. Bicarburetted hydrogen combines with anhydrous sulphuric acid, forming a white compound, fusible at about  $176^\circ$ , and of the formula  $C_4H_4,4SO_3$ , which has been improperly called *sulphate of carbyle*. In order to prepare it, olefiant gas, totally free from ether, and vapours of anhydrous sulphuric acid, are passed simultaneously into a U-tube, when the combination takes place with great elevation of temperature, while the substance, which is at first liquid, solidifies into a radiated crystalline mass on the sides of the tube. In order to purify it, it is left for several days in vacuo, over a cup containing caustic potassa, which absorbs the vapours of the anhydrous sulphuric acid.

The same product is formed by placing an open tube containing absolute alcohol in a bottle containing anhydrous sulphuric acid, and allowing the bottle, after being well corked, to rest for several days. The vapours of alcohol and sulphuric acid combine and sulphate of carbyle is formed, but the latter is injured by hydrated sulphuric acid, from which it is freed with difficulty. The reaction in this case is expressed by the following equation:



*Sulphate of carbyle* absorbs moisture from the air; and if the absorption take place slowly, and without any elevation of temperature, a peculiar acid, called *ethionic*, is obtained, of which the formula is  $C_4H_6O,4SO_3$ . This acid forms, with baryta, a salt soluble in water but insoluble in alcohol; and it yields crystallizable salts with the majority of bases.

By boiling the solution of ethionic acid for a few moments, or by dissolving the sulphate of carbyle in hot water, a new acid, called *isethionic*, is obtained, presenting the same composition  $C_4H_6O,2SO_3$  as sulphovinic acid, while the liquid contains free sulphuric acid. Isethionic acid differs from sulphovinic acid by being much more fixed, as its solution may be boiled indefinitely without undergoing any change. Isethionates are also much more stable than sulphovinates, for they bear without decomposition temperatures of  $400^\circ$  or  $550^\circ$ .

#### *Action of Chlorine, Bromine, and Iodine on Bicarburetted Hydrogen.*

§ 1336. By causing chlorine in greater or less quantity to act upon bicarburetted hydrogen, and under the influence of a more or less intense degree of light, various products result, which shall be mentioned: if both gases, moist, and in nearly equal volumes, be introduced into a large flask exposed to the diffuse light of day, they combine with evolution of heat, and an oleaginous liquid trickles down the sides of the flask. If the gases were dry, reaction would ensue under the influence of direct solar light.

When any considerable quantity of this product is to be prepared, the apparatus must be arranged as represented in fig. 677. A is a large retort, in which is prepared the olefiant gas which traverses the washing bottle B containing concentrated sulphuric acid, which retains the vapours of alcohol and ether, and then the bottle C con-

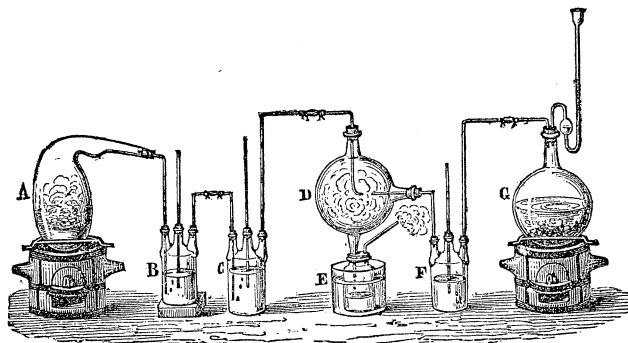


Fig. 677.

taining a solution of potassa to absorb the sulphurous and carbonic acids; whence it passes into a flask D having 3 tubulures, which also receives the chlorine disengaged from the flask G, having been made to traverse the water in the bottle F. The ends of the tubes which convey the two gases into the flask D are placed opposite to each other, so that the gases may mix immediately; while the liquid formed falls through the lower part of the flask into a well-cooled bottle E; the excess of gas escaping by the same tubulure. The liquid obtained is shaken several times with water, and then distilled again and again, alternately with sulphuric acid and potassa, which destroy a small quantity of the foreign substances produced by the reaction of chlorine on the vapour of ether which accompanies olefiant gas when the evolution of the gas is too rapid. If the operation be continued for a long time, by exhausting the action of the sulphuric acid on the alcohol, it frequently happens toward the close that the potassa of the bottle C passes into the state of bisulphite of potassa, and the sulphurous acid is no longer absorbed; in which case a certain quantity of chlorosulphuric acid (§ 132) is obtained intimately mixed with the principal product. The liquid condensed in the bottle E, which then possesses a sulphurous, acid, and extremely penetrating odour, becomes heated when it is shaken with water, and yields a large quantity of sulphuric and chlorohydric acids, arising from the decomposition of the chlorosulphuric acid. It is important to remark that chlorine and sulphurous acid, alone, do not combine in the presence of the most intense solar rays, while in the presence of bicarburetted hydrogen



the combination takes place in diffuse light. The chlorine and bicarburetted hydrogen, which, when dry, exert no action on each other in diffuse light, combine, on the contrary, very readily, when sulphurous acid exists in the mixture; the latter then forming chlorosulphuric acid with a portion of the chlorine. The formation of one of these compounds assists, therefore, the production of the other.

The product resulting from the combination of 1 vol. of chlorine with 1 vol. of olefiant gas, which has long been known under the name of *Dutch liquid*, because it was discovered by an association of chemists in Holland, is a colourless liquid, of an agreeable odour. Its density is 1.280 at 32°, and it boils at 184.1°. The density of its vapour being 3.45, its composition is represented by the formula  $C_4H_4Cl_2$ , which corresponds to four volumes of vapour, but it is generally written  $C_4H_3Cl, HCl$ , from the manner in which the substance behaves with an alcoholic solution of potassa.

§ 1337. Dutch liquid is not decomposed by an aqueous solution of potassa, and may be distilled with it without any apparent change; while if it be dissolved in an alcoholic solution of potassa, it is immediately decomposed, and a large quantity of chloride of potassium is deposited, while the alcohol contains in solution a new and very volatile substance. In order to separate it, the liquid must be distilled in a water-bath slightly heated, and the gas disengaged must be passed first through an apparatus containing concentrated sulphuric acid, which retains the vapours of the alcohol, and then into a receiver reduced to a low temperature by a mixture of ice and chloride of calcium. A very volatile liquid condenses in the receiver, boiling below 32°, having a sharp and slightly alliaceous smell, and of which the composition corresponds to the formula  $C_4H_3Cl$ , represented by 4 vol. of vapour. The composition of this substance is exactly the same as that of bicarburetted hydrogen, except that 1 equiv. of hydrogen is replaced by 1 equiv. of chlorine. Dutch liquid may itself be considered as a combination of the substance  $C_4H_3Cl$  and chlorohydric acid. When the chlorine reacts on the bicarburetted hydrogen, 1 equivalent of chlorine abstracts 1 equivalent of hydrogen to form 1 equivalent of chlorohydric acid, while the place thus made empty in the molecule of olefiant gas is immediately filled by 1 equivalent of chlorine, forming 1 equivalent of *monochlorinated bicarburetted hydrogen*, which remains in combination with the equivalent of chlorohydric acid formed.

§ 1338. The action of chlorine on bicarburetted hydrogen is not confined to the abstraction of but one equivalent of hydrogen and its replacement by 1 equiv. of chlorine; and the other three equivalents of hydrogen may successively be replaced by a corresponding number of equivalents of chlorine, thus furnishing the series of products:

$C_4H_4$  and their compounds with chlorohydric acid.

$C_4H_3Cl$	“	“	$C_4H_3Cl, HCl.$
$C_4H_2Cl_2$	“	“	$C_4H_2Cl_2, HCl.$
$C_4HCl_3$	“	“	$C_4HCl_3, HCl.$
$C_4Cl_4$	“	“	$C_4Cl_4, HCl.$

On passing dry chlorine through Dutch liquid, the latter will be found to dissolve it largely, and if the bottle be then placed in the sun, a powerful reaction ensues, a large quantity of chlorohydric acid being disengaged, while the liquid is completely discoloured; and by repeatedly saturating it with chlorine, and exposing it to the rays of the sun, at properly regulated intervals, Dutch liquid may be converted into a less volatile product, which boils at  $239^\circ$ , and of which the density in the liquid state is 1.422, while that of its vapour is 4.60. The formula of this substance being  $C_4H_3Cl_3$ , it will be recognised as Dutch liquid, in which 1 equiv. of hydrogen is replaced by 1 equiv. of chlorine. The same product is formed when chlorine is caused carefully to act upon monochlorinated bicarburetted hydrogen  $C_4H_3Cl$ , but it is more easily obtained by passing the latter substance in the state of gas through the perchloride of antimony  $Sb_2O_5$ , which dissolves it freely. When the perchloride of antimony is saturated, it is distilled, and a colourless liquid, consisting of  $C_4H_3Cl_3$ , or *monochloruretted Dutch liquid*, is collected. The formula of this substance may be written  $C_4H_2Cl_2, HCl$  for the same reasons which have been stated for Dutch liquid. In fact, on dissolving monochlorinated Dutch liquid in an alcoholic solution of potassa, a precipitate of chloride of potassium is formed, and a liquid of which the formula is  $C_4H_2Cl_2$  separates by distillation. The density of this liquid, which may be considered as *bichlorinated bicarburetted hydrogen*, is 1.250, and it boils between  $95^\circ$  and  $104^\circ$ . The density of its vapour 3.35, and the equivalent  $C_4H_2Cl_2$  therefore correspond to 4 vol. of vapour like that of olefiant gas.

By operating on monochlorinated Dutch liquid  $C_4H_3Cl_3, HCl$ , in the same manner as has been explained for the original liquid  $C_4H_3Cl, HCl$ , the chlorine again abstracts hydrogen in the state of chlorohydric acid, while a substance results which may be considered as *bichlorinated Dutch liquid*, and of which the formula is  $C_4H_2Cl_4$ . The density of this substance is 1.576: it boils at  $275^\circ$ , the density of its vapour being 5.79, so that the equivalent  $C_4H_2Cl_4$  is again represented by 4 vol. of vapour.

We shall write the formula of this product  $CHCl_3, HCl$ , because, in contact with an alcoholic solution of potassa, it is decomposed into chlorohydric acid, which combines with the potassa, and into a new substance  $C_4HCl_3$ , which is *trichlorinated bicarburetted hydrogen*.

Bichlorinated Dutch liquid, subjected again to the action of chlorine in the manner above indicated, is converted into *trichlorinated Dutch*

liquid  $C_4HCl_5$ , which boils at  $307^\circ$ , and the density of which at  $32^\circ$  is 1.663, while that of its vapour is 7.08, and the equivalent  $C_4HCl_5$  is therefore still represented by 4 vol. of vapour. The formula  $C_4HCl_5$  may be written  $C_4Cl_4.HCl$ , because this substance, in contact with an alcoholic solution of potassa, is decomposed and yields the product  $C_4Cl_4$ , which should be considered as *quadrichlorinated* or *perchlorinated bicarburetted hydrogen*, all the hydrogen of the olefiant gas being here replaced by an equivalent quantity of chlorine, while the new substance is a simple chloride of carbon, but its composition is still the same as that of bicarburetted hydrogen, since its formula corresponds to 4 vol. of vapour.

The density of chloride of carbon  $C_4Cl_4$  is 1.61: it boils at  $251.6^\circ$ .

Finally, by treating trichlorinated Dutch liquid  $C_4HCl_5$  with an excess of chlorine, in the sun, it loses the last equivalent of hydrogen, which is replaced by 1 equiv. of chlorine, when a chloride of carbon  $C_4Cl_6$ , which may be considered as *quadrichlorinated* or *perchlorinated Dutch liquid*, is formed. This chloride of carbon, sometimes called *sesquichloride of carbon* on account of its composition, is solid and crystalline, having a peculiar aromatic smell, and is readily purified by dissolving it in boiling alcohol, when the liquid deposits the chloride of carbon, on cooling, in the form of small white crystals, which melt at  $320^\circ$ , while the substance boils at  $356^\circ$ . The density of its vapour being 8.16, the equivalent  $C_4Cl_6$  is therefore represented by 4 vol. of vapour.

The chloride of carbon  $C_4Cl_4$ , of the series of bicarburetted hydrogen, combines readily with chlorine, and is converted into solid chloride of carbon  $C_4Cl_6$ , of the series of Dutch liquid; while, reciprocally, the chloride of carbon  $C_4Cl_6$  is readily transformed into chloride of carbon  $C_4Cl_4$ . By passing the vapour of the chloride of carbon  $C_4Cl_6$  through a tube heated to redness, it is converted into chloride of carbon  $C_4Cl_4$  and chlorine; but it is difficult by this method to obtain the chloride  $C_4Cl_4$  pure, on account of the facility with which it combines with chlorine when it passes with the latter gas into the receiver in which it is condensed. This transformation is more readily effected by dissolving the chloride of carbon in an alcoholic solution of sulphhydrate of sulphide of potassium, when a very energetic reaction ensues if it be slightly heated, while a large quantity of sulphydric acid is disengaged. The chloride of carbon should be added by small quantities at a time, and too great an excess of sulphhydrate of sulphide of potassium must be avoided. When the solution of gas ceases, the alcoholic liquor collected in the receiver is distilled and diluted with water, when the chloride of carbon  $C_4Cl_4$  is deposited in the form of a colourless liquid.

§ 1339. There exist, therefore, two series of products derived from two original substances, bicarburetted hydrogen  $C_4H_4$  and Dutch liquid  $C_4H_4Cl_2$ , by the successive substitution of equivalent quantities of chlorine for hydrogen, while Dutch liquid itself may be considered

as being derived, by the same mode of generation, from a carburetted hydrogen  $C_4H_6$  as yet unknown.

In proportion as the chlorine thus replaces the hydrogen, the density of the substance increases, and its boiling point rises; which relations are easily seen in the following tables:

*Series of Bicarburetted Hydrogen.*

Bicarburetted hydrogen $C_4H_4$ ,	gas does not liquefy at any temperature.
Monochlorinated bicarburetted hydrogen... $C_4H_3Cl$ ,	boils at about $14^\circ$ .
Bichlorinated bicarburetted hydrogen..... $C_4H_2Cl_2$ ,	boils at $95^\circ$ , density 1.250.
Trichlorinated bicarburetted hydrogen..... $C_4HCl_3$ ,	“ “ “ “
Quadrichlorinated bicarburetted hydrogen $C_4Cl_4$ ,	“ $251.6^\circ$ , “ 1.619.

*Series of Dutch Liquid.*

Carburetted hydrogen (unknown)..... $C_4H_6$ .	
Dutch liquid..... $C_4H_4Cl_2$	boils at $180.5^\circ$ , density 1.256.
Monochlorinated Dutch liquid..... $C_4H_3Cl_3$	“ $239^\circ$ , “ 1.422.
Bichlorinated Dutch liquid..... $C_4H_2Cl_4$	“ $275^\circ$ , “ 1.576.
Trichlorinated Dutch liquid..... $C_4HCl_5$	“ $307.4^\circ$ , “ 1.619.
Quadrichlorinated Dutch liquid..... $C_4Cl_6$	“ $356^\circ$ .

In all these products, the equivalent is represented by 4 volumes of vapour, and it may be admitted that the substances of the same series present the same *molecular grouping*, and only differ from each other in the chemical nature of one of their elements, hydrogen, which is more or less completely replaced by equivalent quantities of chlorine.

§ 1340. Bromine also combines with bicarburetted hydrogen, and yields a substance  $C_4H_4Br_2$  which corresponds exactly to Dutch liquid. It is prepared by dropping bromine into a current of bicarburetted hydrogen; when the bromine is almost instantaneously discoloured and converted into an ethereal liquid, the odour of which resembles that of Dutch liquid. In order to purify it, it is washed with a small quantity of water, and then distilled several times, alternately, over concentrated sulphuric acid and baryta. The density of the liquid is 2.16 at  $69.8^\circ$ ; it boils at  $271.4^\circ$ , and solidifies at  $55.4^\circ$  into a white crystalline mass resembling camphor. Its equivalent is represented by 4 volumes.

The product  $C_4H_4Br_2$  undergoes, by distillation with an alcoholic

solution of potassa, a decomposition analogous to that experienced by Dutch liquid; bromide of potassium and a gas  $C_4H_3Br$ , which condenses readily in a mixture of ice and sea-salt, being formed. It is *monobrominated bicarburetted hydrogen*, and its density is about 1.52, while the density of its vapour is 3.64, and its equivalent is represented by 4 volumes of vapour.

Bromine attacks monobrominated bicarburetted hydrogen, and converts it into a liquid  $C_4H_3Br_3$  which corresponds to monochlorinated Dutch liquid. The action of bromine does not appear to extend any further, even by long exposure to the rays of the sun.

§ 1341. If bicarburetted hydrogen be passed to the bottom of a matrass containing iodine and heated to  $120^\circ$  or  $140^\circ$ , the iodine soon fuses, and yellowish needles, which become completely white by the prolonged action of the olefiant gas, condense in the neck of the matrass; by treating which with alkaline or ammoniacal water, a crystalline substance  $C_4H_4I_2$  is obtained corresponding to Dutch liquid. This substance becomes slightly yellow by drying, but recovers its whiteness when exposed to a current of bicarburetted hydrogen. It has an ether-like, sharp, and penetrating odour, causing a flow of tears; and light decomposes it spontaneously. It melts at  $167^\circ$ , but is destroyed at a temperature slightly above that point. Potassa dissolved in alcohol decomposes it, and produces *moniodinated bicarburetted hydrogen*  $C_4H_3I$ , which is a volatile liquid; while the greater part of the product is still further decomposed and yields a gaseous carburetted hydrogen.

By decomposing Dutch liquid by alcoholic solutions of monosulphide of potassium, solid products result, in which the sulphur replaces the chlorine of the original substances; but these products have been but little studied, and as yet only the compound  $C_4H_4S_2$ , which corresponds to Dutch liquid, is known with certainty.

#### *Oil of Wine.*

§ 1342. During the preparation of ether or bicarburetted hydrogen by the reaction of concentrated sulphuric acid on alcohol, a certain quantity of a very heavy oily substance, called *heavy oil of wine*, which dissolves in ether, but separates from it when it is diluted with a sufficient quantity of water, is constantly formed. The best method of preparing it consists in heating 1 part of absolute alcohol and  $2\frac{1}{2}$  parts of concentrated sulphuric acid, and first collecting the products in a bottle kept at the temperature of  $95^\circ$  or  $104^\circ$ , in which very little ether, but the greater portion of the heavy oil of wine condenses; and then in a second cold receiver, if the ether is to be preserved. The same substance is obtained by decomposing by heat well-dried sulphovates. It is washed several times with cold water, in order to remove the alcohol, ether, the sulphurous and sulphuric acids which impurify it, and then exposed for several days in vacuo over concentrated sulphuric acid, in order

to absorb the water. It is, however, difficult to obtain a uniform composition of the substance, and chemists are not agreed as to its nature. From analyses most worthy of confidence, its formula would be  $C_5H_9O, 2SO_3$ , although it may possibly be true *sulphuric ether*  $C_4H_5O, SO_3$ , belonging to the series of compound ethers of which we are about to treat, and mixed with a small quantity of foreign substances, principally carburetted hydrogen, which may, in fact, be separated from it. It is sufficient to digest heavy oil of wine for some time with hot water, or better still, with an alkaline liquid, in order to decompose it into sulphovinic acid and a light oil having the same elementary composition as bicarburetted hydrogen, but the boiling point of which is as high as  $536^\circ$ . It is not yet decided whether this latter substance is a product of the decomposition of heavy oil of wine, or if it be merely mixed with it. This oily carburetted hydrogen, allowed to rest for some time, deposits crystals which are purified by pressing them between tissue-paper, and the composition of which is the same as that of liquid carburetted hydrogen: they melt at  $230^\circ$ , and distil at  $320^\circ$ .

#### COMPOUND ETHERS AND VINIC ACIDS.

§ 1343. The action of acids on alcohol calls into existence numerous compounds, formed by the combination of 1 equiv. of ether  $C_4H_5O$  with 1 or 2 equiv. of acid. Compounds containing 2 equiv. of acid are powerful acids, which accurately saturate the bases, and form a great number of crystallizable salts, and they are commonly called *vinic acids*; sulphovinic acid, the preparation and properties of which we have described, (§ 1330,) belonging to this class. The compounds containing only 1 equiv. of acid are neutral with reagents, and are called *compound ethers*.

Certain acids, such as oxalic and carbonic, form both compounds, while others, as phosphoric, form only the acid compound, vinic acid; and, lastly, others, as nitric and acetic, yield the neutral compound alone. The majority of compound ethers may be distilled without alteration, but are decomposed by being boiled with an alkaline solution; the acid of the compound ether generally combining with the alkali, while the ether  $C_4H_5O$  set free combines with 1 equiv. of water to form alcohol. Nearly all the known acids are capable of forming with alcohol compound ethers or vinic acids; and we shall now describe such of these compounds as are formed by mineral acids and some organic acids already described, and shall refer the study of the others to those chapters in which the properties of the acid entering into their composition is to be described.

We shall not again touch on sulphovinic acid, which has been sufficiently described, (§ 1330;) and the neutral compound, *sulphuric ether*  $C_4H_5O, SO_3$ , has hitherto not been obtained.\*

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\* It was recently formed by Dr. C. Wetherill.—*J. C. B.*

*Phosphovinic Acid*  $(C_4H_5O + 2HO), PO_5$ .

§ 1344. Phosphovinic acid is obtained by heating for some time, at a temperature of  $176^\circ$ , equal parts of absolute alcohol and a syrupy solution of phosphoric acid; after which the liquid is allowed to rest until the following day, when it is diluted with water and saturated with carbonate of baryta, when the free phosphoric acid forms an insoluble phosphate with baryta, while the phosphovinate produced with this base is soluble. The solution, when evaporated, deposits, on cooling, crystals of phosphovinate of baryta, which is much less soluble than the sulphovinate: at  $104^\circ$ , its greatest point of solubility, 100 parts of water dissolve only 9.3. It is also much more fixed than the sulphovinate, for it may be heated up to  $570^\circ$  without change. By dropping sulphuric acid into a solution of phosphovinate of baryta, the baryta is precipitated and a solution of phosphovinic acid obtained, which may be boiled without alteration, and which, when evaporated to the consistence of syrup in the vacuum of an air-pump, deposits crystals, if the temperature be low. The majority of the phosphovinates being soluble in water, are easily prepared by double decomposition, by pouring the sulphate of the base into a solution of phosphovinate of baryta.

Crystallized phosphovinate of baryta contains 12 equiv. of water of crystallization, which may be driven off by heat without alteration. The formula of the dried salt is  $(2BaO + C_4H_5O), PO_5$ ; and it presents, therefore, the composition of the tribasic phosphates, by admitting that ether  $C_4H_5O$  replaces 1 equiv. of base. The compositions of the other phosphovinates are analogous.

No neutral compound of ether with phosphoric acid is known.

*Nitric Ether*  $C_4H_5O, NO_5$ .

§ 1345. Nitric acid forms with ether only a neutral compound, *nitric ether*; no vinic acid having hitherto been discovered.

On mixing alcohol with nitric acid and heating it gently, a violent reaction ensues, and a large quantity of nitrous gas is disengaged, while, together with other products, there results an ether which is not nitric ether  $C_4H_5O, NO_5$ , but *nitrous ether*  $C_4H_5O, NO_3$ . Nitric ether may, however, be produced by the direct action of nitric acid on alcohol, if the forming of nitrous acid be avoided, because this acid, on account of its more powerful oxidizing agency, yields very complicated products. It is effected by gently heating in a retort 150 gm. of a mixture of equal parts of alcohol at  $0.85^\circ$  and very pure concentrated nitric acid, of the density of 1.4, to which is added 1 gm. of *urea*, an organic substance which shall be described among the products of the animal economy. The first product of distillation is composed chiefly of alcohol diluted with water, but the nitric ether itself very soon distils over, and, toward the close of the operation, this liquor forms a denser layer at the bottom of the

receiver. The operation is arrested when about  $\frac{1}{8}$  of the liquid still remains in the retort; and in order to separate that which is dissolved in the supernatant alcoholic liquor, water is added to it and it is shaken; after which the ether is decanted, washed with an alkaline solution, then with water, and, lastly, it is distilled over chloride of calcium.

The object of the small quantity of urea added to the mixture is to prevent the formation of nitrous acid, or rather to effect the destruction of this acid as fast as it is formed. The urea combines with the nitric acid and constitutes nitrate of urea, which compound is readily destroyed by contact with nitrous acid, the two substances being converted into nitrogen, water, and carbonic acid. Nitric ether has a pleasant and sweet smell, and a saccharine taste: its density is 1.112, and it boils at  $185^{\circ}$ , decomposing at a temperature slightly above its boiling point, and forming explosive vapour when heated above  $212^{\circ}$ . An aqueous solution of potassa does not decompose nitric ether, but an alcoholic solution of potassa destroys it, even when cold, alcohol and nitrate of potassa being formed.

*Nitrous Ether*  $C_4H_5O, NO_3$ .

§ 1346. It has just been said that nitrous ether is one of the products of the action of ordinary nitric acid on alcohol, but the reaction is extremely tumultuous, and if large quantities of the mixture are operated on, especially when in a small-necked retort, an explosion may ensue. The best method of preparing it consists in pouring carefully into a bottle, by means of a funnel terminating in a narrow tube descending to the bottom of the bottle, first, one part in volume of alcohol of 0.85, then one part of nitric acid with 4 equiv. of water. The bottle, loosely corked in order to allow the gases to escape, is left for 2 or 3 days in as cold a place as possible, when the upper layer, which contains a large quantity of nitrous ether, is decanted, and then agitated with a weak solution of caustic potassa, and digested with chloride of calcium.

Pure nitrous ether is colourless, and its odour resembles that of pippin apples, while its density is 0.886, and it boils at about  $69.8^{\circ}$ .

*Sulphurous Ether*  $C_4H_5O, SO_2$ .

§ 1347. This compound ether is not formed by the direct action of sulphurous acid on alcohol, or on a mixture of alcohol and sulphuric acid, but is obtained by pouring alcohol on protochloride of sulphur, when the mixture becomes heated, while chlorohydric acid is disengaged and sulphur deposited. By distillation, alcohol first passes over, and then, when the temperature approaches  $338^{\circ}$  a colourless liquid, having the smell of mint, and the density 1.085, and which is *sulphurous ether*  $C_4H_5O, SO_2$ . It decomposes slowly in a moist atmosphere.



*Boracic Ether*  $C_4H_5O, 2BO_3$ .

§ 1348. On mixing equal weights of fused and finely powdered boracic acid, and absolute alcohol, a considerable quantity of heat is evolved; and if the mixture be distilled in a retort furnished with a thermometer, alcohol first passes over, while the temperature gradually rises and soon exceeds  $212^\circ$ . The distillation is arrested when the temperature reaches  $230^\circ$ ; and the mass, when cooled, is dissolved in ether, the ethereal solution is evaporated, and the viscous residue heated to  $392^\circ$  in an oil-bath; when the substance remaining is *boracic ether*. It is a transparent glass, somewhat soft at the ordinary temperature, and which, at the temperature of  $104^\circ$  or  $120^\circ$ , may be drawn out into thread. It smells feebly of ether, and at  $392^\circ$  it yields white vapours, while a temperature of  $570^\circ$  decomposes it, disengaging very pure bicarburetted hydrogen. Tepid water also decomposes it, forming alcohol and boracic acid. Alcohol and ether dissolve boracic ether and form solutions which set into gelatinous masses on the addition of water. When an alcoholic solution of boracic ether is distilled, a considerable quantity of it is carried over by the alcoholic vapours, which then burn with a beautiful green flame, owing to the presence of boracic acid.

*Silicic Ethers*  $3C_4H_5O, SiO_3$  and  $3C_4H_5O, 2SiO_3$ .

§ 1349. When absolute alcohol is carefully poured into chloride of silicium, a very energetic reaction ensues, and a large quantity of chlorohydric acid gas is generated. Alcohol is gradually added until a new addition produces no evolution of gas; and on then distilling the mixture, chlorohydric ether is first disengaged, and the temperature in the retort soon rises to  $320^\circ$ , while the greater portion of the substance distils between  $320^\circ$  and  $338^\circ$ , which is separately collected. When the temperature exceeds  $338^\circ$  the receiver is changed, and distillation is carried to dryness. The product distilled between between  $320^\circ$  and  $338^\circ$  is again rectified, and then is almost entirely composed of a liquid boiling between  $323.5^\circ$  and  $325.5^\circ$ , and of which the formula is  $3C_4H_5O, SiO_3$ . It is a silicic ether, differing in composition from the compound ethers hitherto described, in containing 3 equiv. of ether  $C_4H_5O$  for 1 equiv. of silicic acid. Silicic ether is a colourless liquid, of an ether-like and penetrating smell, of a taste like pepper, and of the density 0.942. Water does not dissolve it, but decomposes it after a time, and silicic acid is separated. When silicic ether is left for a very long time in a badly-stoppered bottle, decomposition is gradually effected at the expense of atmospheric moisture, the silicic ether becoming more and more viscous, while it still preserves its transparency, while there remains at last a perfectly transparent, vitreous mass, of great hardness, consisting of hydrated silicic acid.

By again rectifying the products of the action of alcohol on chloride of silicium which have distilled above  $392^{\circ}$ , and collecting separately the product which distilled above  $572^{\circ}$ , a new ether of the formula  $3C_4H_5O, 2SiO_2$  is obtained. The formula of the two silicic ethers differ greatly from those of other compound ethers. It has been seen (§ 244) that chemists are not agreed upon the equivalent of silicium and the formula of silicic acid, and that some think that the formula should be written  $SiO$ ; in which case the two silicic ethers would assume the formula  $C_4H_5O, SiO$  and  $C_4H_5O, 2SiO$ , the former being analogous to that of ordinary compound ethers, and the latter to that of vinic acids.

*Carbonic Ether*  $C_4H_5O, CO_2$  and *Carbovinic Acid*  $C_4H_5O, 2CO_2$ .

§ 1350. Carbonic ether is not obtained by the direct action of carbonic acid on alcohol, but has been produced by distilling oxalic ether with potassium. The oxalic ether is introduced into a tubulated retort and heated, potassium or sodium being gradually added until gas, consisting of carbonic oxide, is no longer evolved. The colour of the substance remaining in the retort is of a deep red; and when it is again distilled with a quantity of water, the carbonic ether forms the upper layer of the distilled liquid, which is decanted and redistilled over chloride of calcium.

Carbonic ether is a colourless, very fluid liquid, of an aromatic smell and acrid taste, and its density is 0.975, while it boils at  $258.8^{\circ}$ , yielding a vapour of the density 4.1; and its equivalent  $C_4H_5O, CO_2$  is represented by 2 volumes of vapour. Potassa dissolved in alcohol changes it but slightly when cold; while, when hot, carbonate of potassa is formed, and alcohol is separated.

Carbonic ether is decomposed by a solution of ammonia, and yields alcohol, and a white crystalline substance soluble in water and alcohol, to which the name of *urethan* has been given. The formula of urethan is  $C_4H_5O, (C_2O_3, NH_2)$ ; and it may be regarded as a compound ether, formed by a peculiar acid  $C_2O_3, NH_2$ , which has been called *carbamic acid*; in which case urethan would be *carbamic ether*. We have, in fact,



If a concentrated solution of caustic potassa in anhydrous alcohol be saturated with carbonic acid gas, the liquor at last sets into a mass, in consequence of a copious deposit of carbonate, bicarbonate, and *carbovinate* of potassa. Ether, which completes the precipitation of the carbovinate of potassa, is poured into the flask, and after having decanted the liquor, the deposit is shaken with absolute alcohol, which dissolves only the carbovinate. The alcoholic solution is filtered and dropped into very anhydrous ether, which again precipitates the carbovinate of potassa. The formula of the salt, dried in vacuo, is  $KO, (C_4H_5O, 2CO_2)$ ; and it forms white, pearly

spangles, greasy to the touch. Water decomposes it instantly into alcohol and bicarbonate of potassa.

*Oxychlorocarbonic Ether*  $C_4H_5OC_2O_3Cl$ .

§ 1351. On pouring absolute alcohol into a matrass filled with chlorocarbonic gas,  $COCl$  (§ 258,) the temperature rises, and the liquid separates into two layers, the lower of which is formed of oxychlorocarbonic ether. It is purified by digesting it over litharge or chloride of calcium, and then distilling it.

This ether is liquid, colourless, having a penetrating odour, which excites to tears; and its density is 1.133, while it boils at  $201.2^\circ$ , and burns with a green flame. Boiling water decomposes it; and it may be considered as a compound of carbonic ether  $C_4H_5O, CO_2$  and chlorocarbonic gas  $COCl$ . Ammonia decomposes it, chlorohydrate and carbonate of ammonia, and carbonic ether, being formed.

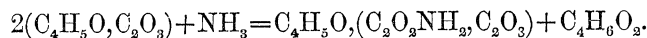
*Oxalic Ether*  $C_4H_5O, C_2O_3$ , and *Oxalovinic Acid*  $C_4H_5O, 2C_2O_3$ .

§ 1352. The best method of preparing oxalic ether consists in mixing in a tubulated retort 1 part of oxalic acid dried at  $212^\circ$ , the formula of which is then  $C_2O_3, HO$ , with 6 parts of absolute alcohol. A thermometer, the bulb of which reaches nearly to the bottom of the retort, is fitted to its tubulure, and the distillation is continued until the thermometer marks  $284^\circ$ , when distilled alcohol is introduced and the distillation repeated, ceasing only when the thermometer marks  $320^\circ$ . The liquid remaining in the retort is then poured into water, when *oxalic ether* separates as a heavy liquid, which, after being washed several times with water, is again distilled over litharge, which seizes upon the free oxalic acid. The product, after being left for some time in contact with fused chloride of calcium, is pure oxalic ether. It is colourless, and of an aromatic odour; and its density is 1.093, while it is very slightly soluble in water, but perfectly so in alcohol. The density of its vapour is 5.078: it boils at  $363.2^\circ$ , and its equivalent  $C_4H_5O, C_2O_3$  corresponds to 2 volumes of vapour.

Oxalic ether is decomposed by contact with a solution of potassa, into alcohol and oxalic acid, which decomposition is also effected, after a long time, by pure water; and when left in a badly-stoppered bottle, in contact with moist air, it deposits crystals of hydrated oxalic acid. Ammonia exerts a remarkable action upon it, forming two new products, *oxamid* and *oxamic ether*.

On dropping oxalic ether into a solution of ammoniacal gas in absolute alcohol, a peculiar substance, first called *oxamethan*, is formed, which is now regarded as a compound ether, formed by a peculiar acid, called *oxamic*,  $C_2O_3NH_2, C_2O_3$ . On evaporating the liquid, the substance separates in the form of lamellated crystals, of a greasy aspect, melting at about  $212^\circ$ , and distilling without change at  $248^\circ$ . It dissolves readily in water and in alcohol, its

aqueous solution being decomposed, by boiling, into binoxalate of ammonia and alcohol. The formula of oxamic ether is  $C_4H_5O, (C_2O_2NH_2, C_2O_3)$ ; and the reaction from which it arises is expressed by the following equation:



It has already been shown that the *oxamid*  $C_2O_2NH_2$  is formed during the distillation of oxalate of ammonia. This substance is more easily prepared by decomposing oxalic ether by an aqueous solution of ammonia. Oxamid is a white crystalline substance, having no action on coloured tests; and cold water does not sensibly dissolve it, while hot water dissolves a small quantity of it, which is again deposited on the cooling of the liquid. Dilute acids and alkalies, when cold, do not affect oxamid; but at the boiling point, oxamid again takes up two equivalents of water, and yields ammonia  $NH_3$ , HO and oxalic acid  $C_2O_3$ .

On adding to oxalic ether dissolved in absolute alcohol a quantity of potassa also dissolved in anhydrous alcohol, in such quantity that it shall saturate one-half of the oxalic acid existing in the ether, a salt almost insoluble in absolute alcohol is precipitated in the form of small crystalline lamellæ, consisting of *oxalovinate of potassa*, which dissolves without alteration in water, but subsequently crystallizes with difficulty. If too great a quantity of potassa be added, oxalate of potassa and alcohol only are obtained. The formula of the salt is  $KO, (C_4H_5O, 2C_2O_3)$ ; and when it is precipitated mixed with a certain quantity of oxalate of potassa, it may be separated from it by treating the precipitate with slightly diluted alcohol, which dissolves only the oxalovinate of potassa. By adding sulphuric acid to this solution, the potassa is precipitated in the state of sulphate, and, if the liquid be then saturated with caustic baryta, a solution of oxalovinate of baryta is obtained. The aqueous solution of oxalovinic acid is readily decomposed by evaporation, and crystals of hydrated oxalic acid are obtained.

#### *Mucic Ether* $C_4H_5O, C_6H_8O_7$ .

§ 1353. Mucic acid does not form a compound ether by its direct action on alcohol, but a mucic ether is obtained by dissolving, with the aid of heat, 1 part of mucic acid in 4 of sulphuric, and then adding to the liquid, when cooled, 4 parts of alcohol. After some time a copious deposit of acicular crystals is formed, which are purified by solution in boiling alcohol, from which they again separate on cooling. The crystals are mucic ether  $C_4H_5O, C_6H_8O_7$ , which melts at about  $284^\circ$ , and is decomposed at  $338^\circ$  without distilling. It dissolves in boiling water, from which it again separates almost entirely on cooling; and boiling alcohol also dissolves it, while after cooling it retains but very feeble traces of it.

*Compounds of Ether  $C_4H_5O$  with the Metallic Chlorides.*

§ 1354. Simple ether forms crystallizable compounds with several metallic chlorides, particularly with the bichlorides of tin and titanium. By introducing into a very dry bottle, containing bichloride of tin or titanium, an open tube containing ether, and allowing the bottle to rest, crystals remarkable for their sharpness, and of which the formula is  $2C_4H_5O, SnCl_2$ ,  $2C_4H_5O, TiCl_2$ , are formed on its sides. The crystals dissolve without change in ether and absolute alcohol, but are decomposed by contact with water, the ether being set free.

*Compound of Ether with Sulphide of Carbon, Sulphocarbvinic Acid or Xanthic Acid  $C_4H_5O, 2CS_2$ .*

§ 1355. These compounds are obtained by dropping into a solution of potassa in absolute alcohol sulphide of carbon until the liquid has lost its alkaline reaction, when a peculiar salt of potassa is formed, the greater portion of which separates in the form of orange-coloured crystals. The composition of the salt corresponds to the formula  $KO, (C_4H_5O, 2CS_2)$ , and it may therefore be regarded as a vinic acid in which the ether  $C_4H_5O$  is combined with sulphocarbonic acid  $CS_2$ : it is also called *xanthic acid*.

The acid is separated by pouring sulphuric or chlorohydric acid into a solution of xanthate of potassa, when the liquid becomes milky, while a colourless oil separates from it, which is several times washed with water. This is *xanthic acid*, which is not very fixed when isolated. The alkaline xanthates are soluble in water, while the other metallic xanthates are insoluble and are precipitated in the form of yellow powders. Xanthates yield, by distillation, several new products, which, however, have not been hitherto sufficiently investigated.

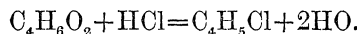
## SIMPLE ETHERS.

§ 1356. The equivalent of oxygen in ether  $C_4H_5O$  may be replaced by respectively 1 equivalent of chlorine, bromine, iodine, sulphur, selenium, tellurium, and cyanogen; and volatile substances may be thus obtained, some of which can form compound ethers and vinic acids. We shall call this class of ethers *simple ethers*; and ordinary ether  $C_4H_5O$  necessarily belongs to it.

*Chlorohydric Ether  $C_4H_5Cl$ .*

§ 1357. This substance is directly formed by the reaction of chlorohydric acid on alcohol. Absolute alcohol, made very cold by being surrounded with ice, is completely saturated with chlorohydric acid gas, and the liquid is then distilled, the gas evolved being conveyed through a washing-bottle containing water and kept at a temperature of  $77^\circ$  or  $86^\circ$ , and thence into a receiver cooled by a re-

frigerating mixture. Chlorohydric ether being gaseous at a temperature above  $55.4^{\circ}$ , traverses the water in the washing-bottle, which retains the excess of chlorohydric acid or alcohol; and condenses in the receiver. In order to remove all traces of alcohol and water, the chlorohydric ether is distilled with concentrated sulphuric acid. The reaction from which it arises is expressed by the following equation:



Chlorohydric ether may also be prepared by heating in a flask a mixture of alcohol at 0.85 and concentrated chlorohydric acid of commerce; the gas being first passed through a washing-bottle containing water, and then through a second containing concentrated sulphuric acid; both bottles being kept at a temperature of  $68^{\circ}$  or  $77^{\circ}$ . It may also be procured by introducing into the flask 12 parts of sea-salt, and then adding a mixture of 1 part of sulphuric acid and 5 parts of alcohol. If the temperature of the laboratory exceed  $59^{\circ}$ , the ether may be collected in the gaseous state in bell-glasses over mercury.

Chlorohydric ether, at a low temperature, is a colourless liquid, of a sharp, slightly alliaceous smell; and its density at  $32^{\circ}$  is 0.291, while it boils at  $54.5^{\circ}$  under the ordinary pressure of the atmosphere. It should be preserved in a vessel the neck of which is hermetically sealed. It dissolves in 50 parts of water at  $32^{\circ}$ , and mixes with alcohol in every proportion. The density of its vapour is 2.235, and its equivalent  $\text{C}_4\text{H}_5\text{Cl}$  corresponds to 4 volumes of vapour. Aqueous alkaline solutions decompose it slowly into alcohol and chlorohydric acid, the decomposition being immediate if the alkali is dissolved in alcohol.

Chlorohydric ether combines with several metallic chlorides, and its compounds may be regarded as compound ethers of the simple ether. It is largely soluble in perchloride of tin, and a definite compound in the form of acicular crystals separates from it. Perchloride of antimony also forms a crystalline compound, but very soon reaction ensues with the formation of protochloride of antimony. Chlorohydric ether also combines with sesquichloride of iron; but all these compounds are destroyed by water, and the chlorohydric ether again becomes free.

Chlorohydric ether is freely absorbed by anhydrous sulphuric acid; a liquid, fuming in the air, and readily decomposed by heat, being formed.

*Bromohydric Ether*  $\text{C}_4\text{H}_5\text{Br}$ .

§ 1358. This ether is prepared by placing in a tubulated retort, furnished with its receiver, 1 part of phosphorus and 40 parts of alcohol at 0.85, and then adding, drop by drop, through the tubulure, 7 or 8 parts of bromine. By the reaction of the bromine on

the phosphorus, in presence of the water contained in the alcohol, phosphorus and bromohydric acid are formed, which latter converts the alcohol into bromohydric ether  $C_4H_9O_2 + HBr = C_4H_9Br + 2HO$ . When the reaction is terminated the retort is heated, still keeping the receiver very cold; and the bromohydric ether is washed with a very weak solution of potassa, and then distilled over chloride of calcium, when it appears as a colourless liquid, having a density of 1.473, at  $32^\circ$ , and boiling at  $105.8^\circ$ .

*Iodohydric Ether  $C_4H_9I$ .*

§ 1359. It is prepared by heating in a retort 5 parts of iodide of phosphorus with 2 parts of alcohol at  $0.85$ , shaking with alkaline water the liquid collected in the receiver, and then distilling over chloride of calcium. Iodohydric ether is a colourless liquid, having a density of  $1.97$  at  $32^\circ$ , and boiling at  $158^\circ$ . Light soon turns it brown, announcing the commencement of decomposition. Its formula  $C_4H_9I$  corresponds to 4 volumes of vapour.

*Cyanohydric Ether  $C_4H_9Cy$ .*

§ 1360. This ether is obtained by distilling a concentrated solution of sulphovinate of baryta with cyanide of potassium, washing the distilled product with water slightly alkaline, and distilling over chloride of calcium. Cyanohydric ether is a colourless liquid having a strongly alliaceous smell, and highly poisonous: its density is  $0.787$ , and it boils at  $179.6^\circ$ . Alkalies dissolved in water decompose it slowly, while oxide of mercury effects a much more rapid decomposition, resulting in cyanide of mercury, cyanohydric acid, and alcohol.

*Sulfhydric Ether  $C_4H_9S$  and its Compound Ethers.*

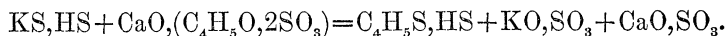
§ 1361. Sulfhydric ether is prepared by passing chlorohydric ether through an alcoholic solution of monosulphide of potassium, after which the liquid is allowed to rest, for 24 hours, in a well-corked bottle, and then distilled; when alcohol, sulfhydric ether, and chlorohydric ether condense in the receiver. This mixture is shaken several times with water, which dissolves the alcohol and chlorohydric ether, and the supernatant fluid, being then separated by means of a pipette, is distilled over chloride of calcium. The first portions which pass over in distillation should be rejected, because they may contain chlorohydric ether.

Sulfhydric ether is a colourless, very volatile liquid, of a penetrating alliaceous smell, to which it is dangerous to be long exposed; and its density is  $0.825$ , while it boils at  $163.4^\circ$ . It is slightly soluble in water, but in all proportions in alcohol. The density of its vapour is  $3.138$ ; and the equivalent  $C_4H_9S$  therefore corresponds to 2 vols. of vapour like ordinary ether  $C_4H_9O$ .

§ 1362. If chlorohydric ether be passed through an alcoholic

solution of sulfhydrate of sulphide of potassium  $\text{KS,HS}$ , and be distilled, a much more volatile liquid is obtained, the composition of which is represented by  $\text{C}_4\text{H}_5\text{S}_2$ ; and which is therefore alcohol  $\text{C}_4\text{H}_5\text{O}_2$  with 2 equiv. of sulphur substituted for 2 equiv. of oxygen. It may be called *sulfhydic alcohol*, and its formula may also be written  $\text{C}_4\text{H}_5\text{S,HS}$ , regarding it as a compound ether of sulfhydic ether  $\text{C}_4\text{H}_5\text{S}$ . It has been called *mercaptan*, on account of its property of combining with oxide of mercury, (*mercurium captans*.)

This compound is also obtained by distilling in a water-bath a mixture of a solution of sulfhydrate of sulphide of potassium and a concentrated solution of sulphovinate of lime. The receiver should, in all cases, be cooled, because the product is very volatile:



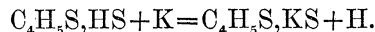
The substance is freed from a small quantity of sulfhydic acid by distilling it over red oxide of mercury.

Sulfhydic alcohol is a colourless liquid, of very disagreeable and penetrating alliaceous smell: its density is 0.84; it solidifies at about  $-7.6^\circ$ , and boils at  $+96.8^\circ$ ; the density of its vapour being 2.14, so that its equivalent  $\text{C}_4\text{H}_5\text{S,HS}$  is represented by 4 volumes, like that of alcohol.

Sulfhydic alcohol forms, with the metallic oxides, compounds in which the hydrogen of the sulfhydic acid is replaced by 1 equiv. of metal, and these compounds have been called *mercaptides*. The most interesting, on account of the facility with which it is produced, is the mercaptide of mercury, which may be called *sulpho-mercuric alcohol*. In order to prepare it, an alcoholic solution of sulfhydic alcohol is gradually poured upon red oxide of mercury, when they combine with elevation of temperature, while a white substance is formed. It is dissolved in boiling alcohol, and, on cooling, separates into white, pearl-like spangles, of which the formula is  $\text{C}_4\text{H}_5\text{S,HgS}$ . This substance melts at about  $185^\circ$ , and decomposes above  $248^\circ$ . Treated with sulfhydic acid it yields sulphide of mercury and sulfhydic alcohol.

If sulfhydic alcohol be poured into an alcoholic solution of acetate of lead, a yellow crystalline precipitate of *sulphoplumbic alcohol*  $\text{C}_4\text{H}_5\text{S,PbS}$  is formed.

When sulfhydic alcohol is heated with potassium, hydrogen is disengaged, and a *sulphopotassic alcohol*  $\text{C}_4\text{H}_5\text{S,KS}$  is formed:



A solution of the product in alcohol yields, on evaporation, a white granular substance; and the salt, when treated with acids, yields a salt of potassa and sulfhydic alcohol. When mixed with an alcoholic solution of chloride of mercury, sulphomercuric alcohol is formed.\*

By distilling a concentrated solution of 2 parts of pentasul-

\* These bodies may be viewed as sulfhydrates conjugate with  $2\text{C}_2\text{H}_2$ .—J. C. B.



phide of potassium  $\text{KS}_5$  with 3 parts of sulphovinate of lime, water and a peculiar ethereal liquid pass over, by washing which with water, and distilling it over chloride of calcium, a liquid results of a very disagreeable alliaceous odour, boiling at  $303.8^\circ$ , and of which the formula is  $\text{C}_4\text{H}_5\text{S}_2$ .

On heating an excess of sulfhydric alcohol with dilute nitric acid the liquor becomes red, from the production of a certain quantity of deutoxide of nitrogen which dissolves in it, but it loses its colour when heated, and after some time an oleaginous liquid separates from it. Nitric acid is gradually added, until the sulfhydric alcohol is entirely decomposed; after which the liquid is diluted with water, and, after having washed the oleaginous substance several times, it is distilled. This new substance is without colour, of an extremely disagreeable odour, of the density 1.24; and it boils at about  $266^\circ$ , but not without alteration. Its composition is represented by the formula  $\text{C}_4\text{H}_5\text{S}, \text{SO}_2$ ; and it would therefore be a compound ether, formed by the combination of sulfhydric ether with sulphurous acid.

When the action of dilute nitric acid on sulfhydric alcohol is prolonged until the oxidizing action ceases, an acid compound is obtained, which forms crystallizable salts with bases; and from the analyses which have been made, the formula of the salt of baryta would be  $\text{BaO}, (\text{C}_4\text{H}_5\text{S}_2\text{O}_4) + \text{HO}$ .

§ 1363. If chlorohydric ether be passed through an alcoholic solution of sulphocarbonate of sulphide of potassium  $\text{KS}, \text{CS}_2$ , a *sulphocarbonic ether*  $\text{C}_4\text{H}_5\text{S}, \text{CS}_2$  which corresponds to carbonic ether  $\text{C}_4\text{H}_5\text{O}, \text{CO}_2$  is formed. After having allowed the substances to act for some time, the liquor is heated to drive off the excess of chlorohydric ether, and it is treated with water; when a liquid of an alliaceous smell, heavier than water, separates from it, which new substance is sulphocarbonic ether  $\text{C}_4\text{H}_5\text{S}, \text{CS}_2$ .

A *sulphocyanohydric ether*  $\text{C}_4\text{H}_5\text{S}, \text{C}_2\text{N}_2\text{S}$  is obtained by distilling a mixture of equal parts of sulphovinate of lime and sulphocyanide of potassium, both in concentrated solution. The product, purified by washing, and then by distillation, is a colourless, very limpid liquid, of the density 1.020, boiling at  $294.8^\circ$ . Its equivalent is represented by 4 volumes of vapour.

#### *Selenohydric Ether* $\text{C}_4\text{H}_5\text{Se}$ .

§ 1364. It is obtained by distilling selenide of potassium with sulphovinate of potassa; but its properties are little known.

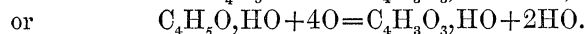
#### *Tellurohydric Ether* $\text{C}_4\text{H}_5\text{Te}$ .

§ 1365. By projecting telluride of potassium into a hot solution of sulphovinate of baryta, and then distilling, a liquid is obtained of a reddish-yellow colour, heavier than water, very poisonous, and

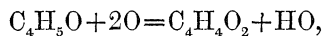
which boils above  $212^{\circ}$ . It is tellurohydric ether; and oxidizes slowly in the air, depositing tellurous acid.

PRODUCTS OF THE OXIDATION OF ALCOHOL AND ETHER.

§ 1366. When alcohol and ether are subjected to a very powerful oxidizing action, they are completely consumed, and converted into water and carbonic acid; while, when the oxidizing action is less powerful, they are converted into acetic acid  $C_2H_3O_2, HO$ , in which case they lose 2 equiv. of hydrogen, which form water with 2 equiv. of oxygen given off by the oxidizing substance, while the 2 equiv. of hydrogen are replaced by 2 equiv. of oxygen, also given off by the oxidizing reagent. We thus have



When the oxidizing action is still more feeble, it is limited to the abstraction of a single equiv. of hydrogen, and to its replacement by 1 equiv. of oxygen, which furnishes *aldehyde*  $C_4H_4O_2$ , according to the formulæ



*Aldehyde*  $C_4H_4O_2$ .

§ 1367. Aldehyde is formed under a number of circumstances, in which alcohol, ether, and the compound ethers are subjected to oxidizing agencies; while the best method of preparing it consists in distilling in a retort, at a gentle heat, a mixture of 6 parts of concentrated sulphuric acid, 4 parts of water, 4 parts of alcohol at 0.80, and 6 parts of finely powdered peroxide of manganese. The retort should only be one-third filled, because the mixture swells considerably during the operation; and a cooling apparatus, through which very cold water passes, and a receiver surrounded by a refrigerating mixture are fitted to the retort. When the reaction appears to be terminated in the retort, the liquid which condensed in the receiver is withdrawn and distilled at two different times over an equal weight of chloride of calcium. The liquid obtained is composed of aldehyde, a small quantity of alcohol and water, and acetic and formic ether. In order to obtain the aldehyde, it is poured into ether saturated with ammoniacal gas; when white crystals, consisting of a combination of aldehyde and ammonia  $NH_3, C_4H_4O_2$  are separated. The crystals are dissolved in their own weight of water, and the solution is introduced into a retort furnished with a receiver cooled by a refrigerating mixture, while sulphuric acid diluted with its volume of water is poured through the tubulure. On distilling it over a water-bath, a liquid is obtained which, when distilled over melted chloride of calcium, yields pure aldehyde.

VOL. II.—2 V

Aldehyde is a colourless, very limpid liquid, of a suffocating odour, and its density is 0.790 at  $64.4^{\circ}$ , while it boils at  $71.3^{\circ}$ , the density of its vapour being 1.479, and its equivalent  $C_4H_4O_2$  therefore corresponding to 2 vol. of vapour. It dissolves, in all proportions, in water, alcohol, and ether, burns with a white flame, and exerts no action on vegetable colours. Aldehyde readily absorbs oxygen from the air, particularly in the presence of water, and is converted into acetic acid, which transformation is effected by all oxidizing agents: thus oxide of silver is reduced by a solution of aldehyde, the metallic silver adhering to the sides of the vessel and covering them with a glittering coating; and nitrate of silver produces the same effect if a small quantity of ammonia be added. Alkalies decompose aldehyde, forming, together with other products, a brown resinous matter, which reaction is often indicated as being characteristic of aldehyde.

Pure and anhydrous aldehyde, preserved for some time in a tube hermetically closed, undergoes isomeric modifications, differing according to the temperature. At  $32^{\circ}$  it is converted into a crystalline, colourless, and transparent substance, which melts at  $35.6^{\circ}$ , and boils at  $201.2^{\circ}$ . The density of its vapour being three times greater than that of aldehyde, its formula may be assumed to be  $C_{12}H_{12}O_6$ . It has been called *elaldehyde*. If, on the contrary, the external temperature range from  $59^{\circ}$  to  $68^{\circ}$ , elongated prismatic crystals, which finally fill the tube, are developed in the aldehyde, and which volatilize at  $248^{\circ}$  without melting. This second isomeric modification of aldehyde has been called *metlaldehyde*, and the density of its vapour is unknown.

Aldehyde is also formed whenever alcohol is burned imperfectly in contact with the air; for example, when that liquid is dropped upon metallic plates heated to  $482^{\circ}$ , or when a wick soaked in alcohol is lighted, and extinguished as soon as the greater portion of the alcohol has evaporated; when the wick is carbonized, and the small quantity of vapour of alcohol which comes in contact with the ignited portions is imperfectly burned, and yields aldehyde, which is known by its suffocating smell. A large quantity of aldehyde is also produced in the experiment of Davy's flameless lamp, (§ 1169.)

When chlorine is passed through diluted and cold alcohol, chlorohydric acid and aldehyde only are formed, the chlorine then exerting an oxidizing agency on the alcohol, by decomposing the water and combining with its hydrogen:  $C_4H_5O, HO + 2Cl + HO = 2HCl + C_4H_4O_2$ .

*Acetic Acid*  $C_4H_3O_3, HO$ .

§ 1368. Alcohol, when pure, or merely diluted with water, does not combine with the oxygen of the air, while the combination is readily effected in the presence of certain substances the chemical elements of which do not interfere, as, for example, very finely di-

vided platinum, which metal may cause the oxidation of a large quantity of alcohol at the expense of the oxygen of the air. In order to perform the experiment, a capsule *a* (fig. 678) containing

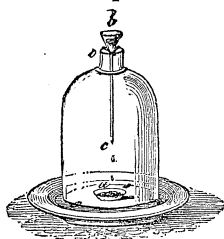


Fig. 678.

platinum-black is placed on a plate, and the capsule is covered with a large bell-glass having an opening *o* at the top, and which rests on three small wooden wedges, to allow the air to enter from beneath; and finally, a funnel *b* having a long and delicate neck *c* is introduced into the opening. By pouring alcohol into the funnel, the liquid drops on the platinum contained in the capsule, and while a slight elevation of temperature ensues, vapours which condense and trickle down the sides of the glass are developed therein. The liquid thus formed on the bottom of the plate is nearly pure acetic acid; but there is produced at the same time, 1st, a certain quantity of aldehyde, easily recognised by its smell; 2dly, a peculiar substance called *acetal*; and 3dly, a small quantity of acetic ether, arising from the reaction of the acetic acid on the undecomposed alcohol.

If the acid liquor be saturated with chalk and distilled, there is obtained in the receiver, water holding in solution aldehyde, acetic ether, and acetal. If this new liquid be digested with its own weight of chloride of calcium, the latter combines with the water and acetic acid, and ethereal liquid separates, which is again distilled, the first portions which pass over being rejected, because they contain a large amount of aldehyde, while the last portions are pure acetal. Acetal is a colourless liquid, boiling at  $167^{\circ}$ , of a density of 0.844, and soluble in water and alcohol. Its composition corresponds to the formula  $C_{14}H_{14}O_4$ , and it may be regarded as being formed by the union in a single group of three molecules of ether, one of them having been modified, under the oxidizing influence, by the substitution of 1 equiv. of oxygen in the place of 1 equiv. of hydrogen,  $3C_4H_5O + 2O = C_{12}H_{14}O_4 + HO$ .

§ 1369. The oxidation of alcohol at the expense of the oxygen of the air is also effected by organic ferments, and in general by all albuminous substances, upon which mysterious action is based the conversion of spirituous liquors into vinegar, that is to say, into acetic acid. Wines of certain vintages, rich in albuminous matter, soon turn sour in the air, and become vinegar; which change new wines undergo much more rapidly than the old, because the latter are freed from albuminous substances, which coagulate and fall to the bottom of the barrel; and therefore, in order to make them ferment, they must be diluted with a small quantity of water and be exposed to the air. What has just been said of wines is equally applicable to other alcoholic liquors, and even to solutions of sugar mixed with yeast and exposed to the air. During the acid ferment-

ation of alcoholic liquors, a mucilaginous substance, which greatly assists this fermentation, is separated, and which, consisting chiefly of albuminous matter, is called the *mother of vinegar*.

In order that acetification may progress rapidly, the alcoholic liquor must be sufficiently diluted with water, and present a large surface to the oxidizing action of the air. These conditions are fulfilled on a large scale by using an alcoholic liquor containing 1 part of alcohol to 8 or 9 parts of water, and adding about  $\frac{1}{1000}$  of fermentable liquor, such as beet-juice, potato-juice, or small beer, when the liquor thus prepared is dropped into barrels (fig. 679) filled with beech shavings. The lower part of the barrel is pierced with several holes *a*, and the upper part with other holes *b*, while a false



Fig. 679.

bottom *cde* forms a vat, into which the alcoholic liquor is poured. The false bottom has a great number of holes, through which pass pieces of twine, having a knob on the end to prevent them from slipping through. The alcoholic liquor flows along the twine, and dropping on the shavings, spreads into a thin layer, and presents a large surface to the oxidizing action of the air, oxidation being effected by means of the ferment contained in the liquor and the albuminous substances in the wood, while

the temperature rises and produces a current of air which enters at the lower holes *a* and escapes through the upper ones *b*. Oxidation is so rapid that when the liquid reaches the bottom of the barrel, it frequently no longer contains any alcohol, but if, after one passage, the alcohol is not completely converted into acetic acid, it is passed through a second time. The presence of acetic acid itself assists the acetic fermentation, for which reason the fresh shavings to be used are previously left for some time in concentrated vinegar. The temperature of the barrel also exerts great influence, and, if it be too cool, heated alcoholic liquor must be added to bring the temperature to between  $86^{\circ}$  and  $97^{\circ}$ .

The acid liquors thus obtained, which constitute common table-vinegar, are dilute solutions of acetic acid, containing in addition the non-fermentable principles which exist in alcoholic liquors. Pure acetic acid is obtained from this liquid by distillation, a very weak acid first passing over, while the following portions contain more acid, and the latter are richer, but are generally deteriorated by the products of the decomposition of foreign substances. The richer liquors are saturated with carbonate of soda, and crystallized acetate of soda is separated by evaporation, and then decomposed

by sulphuric acid, more or less dilute, according to the desired strength of the acetic acid.

§ 1370. Acetic acid is now largely obtained from the acid liquors obtained by the distillation of wood, which yields very complicated products: carbonic acid gas, oxide of carbon, protocarburetted hydrogen, water containing acetic acid in solution, a volatile liquid called *spirit of wood*, some other soluble substances, and, lastly, a black, pitchy portion. The solution of impure acetic acid is called in the arts *pyroligneous acid*; and in order to separate acetic acid from it, it is first saturated with chalk, which furnishes a solution of acetate of lime decomposable by sulphate of soda, acetate of soda and sulphate of lime being formed, which latter, being but slightly soluble, is nearly wholly deposited. The solution is evaporated to dryness, and the residue heated to 400 or 480°, a temperature which does not affect the acetate, but decomposes the empyreumatic substances with which it is mixed. Three parts of roasted acetate of soda being then treated in a distilling vessel with 9.7 of sulphuric acid, the first third of the liquid which distils over, consisting of a weaker acetic acid, is set aside, while the other two-thirds, which are composed of very concentrated acid, always contain a small quantity of sulphuric acid, in order to free the product from which it is distilled over anhydrous acetate of soda. The acetic acid thus obtained, having not yet reached its greatest degree of concentration, is exposed to a low temperature by surrounding with ice, or better still by a refrigerating mixture, the vessels containing it; when the acid, at its maximum of concentration  $C_4H_3O_3.HO$ , sets in a crystalline mass, and the more watery acid is decanted. The crystallized acid is remelted and again cooled, when only one-half of the product is congealed, and the liquid portion being decanted off, the solid acid may be considered as having attained its maximum of concentration.

§ 1371. Acetic acid, monohydrated, or at its maximum of concentration  $C_4H_3O_3.HO$ , is solid at low temperatures, but melts at 60.8°. The acid liquid may be cooled often to 32° and below, without crystallizing, and the bottle may even be shaken without causing crystallization; but if a small glass point be introduced, a crystal is immediately formed at the end of the point, and the whole mass gradually crystallizes; the temperature rapidly rising to 60.8°, and remaining stationary until the solidification is complete. The density of monohydrated liquid acetic acid is 1.063 at 64.4°, and its smell is sharp and penetrating, while its taste is highly acid; but in this state of concentration it exerts a vesicating action and raises blisters on the skin. It boils at 248°, the density of its vapour being 2.09; but it is necessary to measure the density at a very high temperature, because the vapour of acetic acid differs considerably from the laws of permanent gases at temperatures which exceed but slightly its boiling point, (1234.) The equivalent

$C_4H_3O_3,HO$  is represented by 4 volumes of vapour, like that of alcohol.

Acetic acid mixes with water in all proportions; and for the first quantities of water added, the acid liquor acquires a density greater than that of the monohydrated acid; the maximum of density which corresponds to the acid  $C_4H_3O_3+3HO$  being 1.079. By adding larger quantities of water the density diminishes, and the hydrometer can, therefore, not be used to ascertain the strength of acetic liquids.

Chlorine acts powerfully on acetic acid, forming, when the latter is in the monohydrated state  $C_4H_3O_3,HO$  a new acid  $C_4Cl_3O_3,HO$ , called *chloracetic acid*, in which the hydrogen of the anhydrous acid is replaced by an equivalent quantity of chlorine; while, if the acid is further diluted with water, the chlorine exerts an oxidizing action by decomposing the water, and the acetic acid is converted into oxalic and then into carbonic acid.

Ordinary nitric acid acts but feebly on acetic acid, even when assisted by heat.

§ 1372. Acetic acid forms, with bases, a numerous series of salts, several of which are applied in the arts. They are generally soluble in water, and some dissolve in alcohol; and the acid forms frequently several salts with the same base.

All the acetates are decomposed by heat, but the decomposition takes place at very different temperatures, and its products vary according to the nature of the base. The acetates formed by the easily reducible metallic oxides, such as the oxides of silver and mercury, leave a metallic residue, and evolve a portion of their acetic acid unchanged, while another portion of the acid is completely consumed by the oxygen given off by the metallic oxide, and yields water and carbonic acid. The acetates formed by the more powerful bases, as the alkaline acetates, leave as a residue an alkaline carbonate, the acetic acid being converted into a neutral volatile liquid  $C_3H_3O$ , called *acetone*, or *pyroacetic spirit*; which reaction is expressed by the following equation:



Acetates formed by bases of medium strength, as oxide of lead, undergo a complicated decomposition: unchanged acetic acid and acetone are both disengaged at once, while the carbonic acid arising from the portion of decomposed acetic acid is disengaged or remains combined with the base, according to the temperature.

Lastly, when the metallic oxide of moderate strength is easily reduced, as oxide of copper, a portion of the acetic acid is consumed by the oxygen of the oxide, and yields carbonic acid, while the residue of the distillation is composed of metal, or suboxide.

Acetic acid forms two crystallizable salts with potassa: the *neutral acetate*  $KO, C_4H_3O_3$  and the *binacetate*  $KO, C_4H_3O_3 + HO, C_4H_3O_3$ ; the former of which is obtained by saturating acetic acid by car-

bonate of potassa and evaporating the liquor. The salt crystallizes with difficulty and is soluble in water and alcohol; and, if it be dissolved in an excess of acetic acid and evaporated, crystals of the binacetate are obtained, which is deliquescent, melts at  $298.4^{\circ}$ , and at  $392^{\circ}$  yields monohydrated acetic acid, furnishing the means of preparing very pure acid.

*Acetate of soda*  $\text{NaO}, \text{C}_4\text{H}_3\text{O}_3 + 6\text{HO}$ . It has been seen that this salt is prepared on a large scale in the manufacture of wood-vinegar. It crystallizes in large colourless and transparent prisms, which are often remarkable for the great sharpness of their faces. It has a cool and saltish taste, and dissolves in 3 parts of cold water and 5 of alcohol. When heated, it first dissolves in its water of crystallization, but soon parts with it; while, if further heated, it undergoes igneous fusion without decomposition, which begins to ensue only at a degree of heat approaching a dull red.

*Acetate of ammonia*  $(\text{NH}_3, \text{HO}), \text{C}_4\text{H}_3\text{O}_3$ , which is obtained by the direct combination of ammonia with acetic acid, is very soluble in water and alcohol, and is used in medicine. When boiled, it loses a portion of its ammonia and is converted into *binacetate*.

*Acetate of baryta*  $\text{BaO}, \text{C}_4\text{H}_3\text{O}_3 + 3\text{HO}$  forms brilliantly white prismatic crystals, which readily part with 2 equiv. of water at a slightly elevated temperature.

*Acetate of lime* produces only confused crystallizations, resembling cauliflowers.

*Acetate of alumina* is prepared by pouring a solution of sulphate of alumina into a solution of acetate of baryta or lead, until no precipitate is thrown down; and the solution, which then contains acetate of alumina, is used in dyeing. In order to separate the salt from it, the liquor must be evaporated in vacuo, because, when heated, acetic acid is disengaged; when the acetate of alumina remains in the form of a gummy mass, without any appearance of crystallization.

The properties of the acetates of lead and copper, which are of important application in the arts, have already been sufficiently detailed when treating of those metals.

When concentrated acetic acid is poured into a boiling solution of subnitrate of mercury  $\text{Hg}_2\text{O}, \text{NO}_3$ , anhydrous white crystalline lamellæ of *subacetate of mercury*  $\text{Hg}_2\text{O}, \text{C}_4\text{H}_3\text{O}_3$  are deposited on cooling. Red oxide of mercury dissolves readily in acetic acid, and the liquid yields by slow evaporation beautiful colourless crystals of *protoacetate of mercury*  $\text{HgO}, \text{C}_4\text{H}_3\text{O}_3$ , which dissolves without change in cold water, but on boiling deposits perfectly pure red oxide of mercury.

*Acetate of silver*  $\text{AgO}, \text{C}_4\text{H}_3\text{O}_3$  is obtained by dissolving carbonate of silver in acetic acid; and as it is but little soluble in cold water, it may also be prepared by double decomposition, by pouring nitrate



of silver into a solution of acetate of soda. If the liquors are concentrated, the acetate of silver is deposited on cooling.

*Acetic Ether*,  $C_4H_5O, C_4H_3O_3$ .

§ 1373. Acetic ether is formed by the direct reaction of acetic acid on alcohol, but the combination is effected with difficulty, because it is necessary to use anhydrous alcohol and acetic acid at its maximum of concentration, and pour back again into the retort the liquor which has passed over in distillation; and the formation of acetic ether is much more rapid if 10 or 15 per cent. of sulphuric acid be added. The best method of preparing this ether consists in pouring a mixture of 7 parts of concentrated sulphuric acid with 8 of absolute alcohol, or 10 parts of anhydrous acetate of soda, or 20 parts of acetate of lead, into a retort, and distilling as long as any ethereal liquor passes over, the product being collected in a well-cooled receiver. The liquor is poured upon dried pulverized carbonate of soda, which abstracts the greater portion of water from the acetic ether, and combines with the free acetic acid which passes over in distillation. The supernatant liquid stratum is decanted, and distilled over chloride of calcium, which takes up the alcohol; but the complete purification of acetic ether is very difficult, because it combines with chloride of calcium, and forms a crystalline compound, which is destroyed only by the addition of water.

Acetic ether is a colourless, very mobile liquid, of an agreeable ether-like smell, and of the density 0.907 at  $32^\circ$ . It boils at  $165.2^\circ$ , and the density of its vapour is 2.920, its equivalent  $C_4H_5O, C_4H_3O_3$ , being therefore represented by 4 volumes of vapour. It mixes in all proportions with alcohol and ether, and dissolves in 7 parts of water. It is used in medicine.

*Sulphacetic Acid*  $C_4H_4O_4, 2SO_3$ .

§ 1374. By bringing into contact anhydrous sulphuric acid and monohydrated acetic acid  $C_4H_3O, HO_3$ , the two acids combine and form a compound acid. The liquid is diluted with water and saturated with carbonate of baryta, when the free sulphuric acid forms insoluble sulphate of baryta, while the sulphacetic acid yields a soluble sulphacetate of baryta. The liquor, when evaporated, affords crystals of the formula  $2BaO, (C_4H_4O_4, 2SO_3) + HO$ , and which part with their water without decomposition. If the baryta be precipitated from sulphacetate of baryta, by sulphuric acid poured in by drops, or if a solution of sulphacetate of lead be decomposed by sulphhydric acid, an acid liquid results, which on evaporation yields deliquescent crystals, melting at  $143.6^\circ$ , and solidifying in a crystalline mass on cooling. At a more elevated temperature the sulphacetic acid is decomposed.

Crystallized sulphacetic acid, placed, in vacuo, over anhydrous phosphoric acid, gives off one equivalent of water, and then assumes

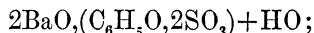
the formula  $C_4H_4O_4, 2SO_3 + 2HO$ ; the 2 equivalents of water which it retains being basic.

*Acetone*  $C_3H_6O$ .

§ 1375. It has been said (§ 1372) that the alkaline acetates yield acetone when they are decomposed by heat; but the best method of preparing it consists in heating a mixture of 2 kilog. of acetate of lead with 1 kilog. of finely powdered quicklime, in an earthen retort, or in the iron bottles used for the transportation of mercury; the temperature being gradually raised to a dull red-heat. The liquor condensed in the receiver is rectified over chloride of calcium, and then allowed to rest for several days on melted chloride of calcium; after which it is distilled, the first  $\frac{3}{4}$  only of the product being collected, while the other fourth contains, besides a still large quantity of acetone, a considerable quantity of a peculiar substance, boiling at  $248^\circ$ , and which has been called *dumasin*.

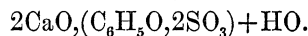
Acetone is a very mobile, colourless liquid, of a peculiar odour; and its density is 0.792, while it boils at  $132.1^\circ$ , the density of its vapour being 2.022; so that its equivalent  $C_3H_6O$  is represented by 2 volumes of vapour. The formula of acetone may be written  $C_6H_6O_2$  or  $C_6H_6O, HO$ , in which case its equivalent is represented by 4 volumes of vapour like that of alcohol. It burns with a brilliant flame; and is soluble in all proportions in water, alcohol, and ether, while chloride of calcium and caustic potassa readily abstract its water.

§ 1376. On mixing acetone with twice its weight of concentrated sulphuric acid, heat is evolved, and the mixture turns brown, while the smell of sulphurous acid is perceived at the same time; and if the liquor be then diluted with water and saturated with carbonate of baryta, insoluble sulphate of baryta is separated, and a soluble salt of baryta, which crystallizes in pearly lamellæ, is obtained. The formula of the salt is



its equivalent of water being removed by drying.

If the acid liquor be saturated with carbonate of lime, a salt of lime is obtained:



If a smaller quantity of sulphuric acid be used, for example, by treating two volumes of acetone with 1 volume of sulphuric acid, a soluble salt of baryta is still obtained by saturating with carbonate of baryta, but which contains only one-half of the sulphuric acid of the preceding acid, and only 1 equivalent of base. The formula of this salt is  $BaO, (C_6H_6O, SO_3) + HO$ .

§ 1377. By distilling 2 volumes of acetone and 1 volume of sul-

phuric acid, two new products result, *mesitylen*  $C_6H_4$  and *mesitic ether*  $C_6H_2O$ .

The mesitylen floats on the surface of the distilled liquid, from which it is separated with a pipette, and shaken several times with pure water, and then distilled over chloride of calcium. Mesitylen is an oleaginous, colourless liquid, of an alliaceous odour, lighter than water, and boiling at  $276.8^\circ$ .

§ 1378. Impure mesitic ether is obtained by treating acetone with sulphuric acid; while it is obtained in a very pure state by decomposing the chlorohydric ether  $C_6H_5Cl$  of acetone by an alcoholic solution of potassa. To effect this, the ether is dissolved in alcohol, and, after having heated it, an alcoholic solution of potassa is added until an alkaline reaction is produced; when, on diluting the liquor with water, an etherized liquid separates, forming the upper stratum, which is drawn off by a pipette, washed several times with water, and distilled over chloride of calcium. It is a colourless liquid, boiling at  $248^\circ$ , insoluble in water, but soluble in alcohol, and its formula is  $C_6H_5O$ .

§ 1379. On passing chlorohydric acid gas through acetone, it dissolves largely in it, and a brown oleaginous liquid results, which is to be digested for some time over litharge to remove the free chlorohydric acid; after which it is washed several times with water, and dried by means of chloride of calcium. This liquid is the *chlorohydric ether of acetone*  $C_6H_5Cl$ , but it is difficult to obtain it pure by this method, and it is more easily effected by pouring into 1 part of acetone, cooled by ice, 2 parts of perchloride of phosphorus  $PCl_5$ , added by small quantities at a time. It is then treated with water, which causes the separation of the chlorohydric ether in the form of a yellow oleaginous liquid. It cannot be distilled, because it is destroyed by heat; and the alkaline liquids decompose it, even water effecting decomposition after some time.

Concentrated nitric acid acts powerfully on acetone, forming several products, the nature of which is, however, not yet sufficiently understood.

§ 1380. From the nature of its compounds, acetone will be seen to resemble alcohol, if its formula be written  $C_6H_6O_2$ . But the acid  $C_6H_5O_2SO_3$ , which may be assimilated with sulphovinic acid, differs from it by saturating 2 equivalents of base, while sulphovinic acid saturates only one. Sulphovinic acid, chlorohydric ether, and the compound ethers of alcohol reproduce alcohol when boiled with alkaline liquids; while the corresponding products of acetone do not yield acetone under the same circumstances. When the vapour of alcohol is passed over hydrated potassa heated to about  $500^\circ$ , acetate of potassa is obtained; but under the same circumstances acetone does not yield an acid corresponding to acetic acid. Lastly, no compound ether has hitherto been obtained with acetone.

*Cacodyl Series.*

§ 1381. By distilling, in a retort furnished with a receiver, a mixture of equal parts of anhydrous acetate of potassa and arsenious acid, a liquid product is obtained, called at first *Cadet's liquid*, then *alcarsin*, and lastly *oxide of cacodyl*; and which ignites when exposed to the air, and possesses many other remarkable properties. The composition of this substance, supposed to be pure, corresponds to the formula  $C_4H_6AsO$ . It behaves in its chemical reactions like the oxide of a radical  $C_4H_6As$ , playing a part analogous to that of cyanogen, and has been called *cacodyl*. This radical enters into a great number of other compounds, as shall presently be described.\*

In consequence of the facility with which this substance changes when exposed to the air, and its poisonous action on the animal economy, great caution must be used in preparing it; and the retort should be hermetically fitted to the receiver, which must be furnished with a tube to conduct the vapours out of the laboratory. At the close of the operation the receiver contains 3 strata of liquid; the middle one, which is brown and of an oleaginous consistence, consists of impure oxide of cacodyl, and is decanted by means of a siphon filled with water, and conveyed to the bottom of a bottle filled with boiled water. It is shaken several times with the water, which is then poured off and replaced by alcohol, which dissolves the oxide of cacodyl. By pouring the alcoholic solution into boiled water, the oxide of cacodyl is again precipitated in the form of a liquid layer at the bottom of the bottle; and the supernatant water being rapidly removed, the access of air is prevented by a rapid current of hydrogen which is passed into the bottle. The latter is then closed, after having introduced into it chloride of calcium intended to absorb the water and alcohol; and the liquid is first decanted in a tubulated retort traversed by a current of hydrogen, and to which a receiver is fitted; and is then distilled, still keeping up the current of hydrogen, when pure oxide of cacodyl is obtained as a colourless, very fluid liquid. It has a strong and very disagreeable smell, is very poisonous, and its density is 1.46. It solidifies at  $-9.4^\circ$ , and boils at about  $302^\circ$ , the density of its vapour being 7.8, and 1 volume of the gaseous substance therefore consisting of

2 vol. of vapour of carbon.....	0.552
6 " hydrogen.....	0.662
$\frac{1}{2}$ " vapour of arsenic.....	5.185
$\frac{1}{2}$ " oxygen.....	1.688
	<hr/> 7.977

and its equivalent  $C_4H_6AsO$  is represented by 2 volumes of vapour.

\* The discovery of cacodyl, and the masterly investigation of all the compounds of this radical, is wholly due to Robert Bunsen.—*W. L. F.*

The chemical reaction which produces it is represented by the following equation :



Oxide of cacodyl is insoluble in water, but it dissolves largely in alcohol and ether. It dissolves phosphorus and sulphur without any change, while chlorine, bromine, and iodine decompose it rapidly. It combines with anhydrous sulphuric acid and forms a crystalline, deliquescent compound, which dissolves in water, yielding an acid liquid.

By pouring a dilute solution of corrosive sublimate into an alcoholic solution of oxide of cacodyl a white precipitate is formed, which is a simple combination of oxide of cacodyl with chloride of mercury, according to the formula  $\text{C}_4\text{H}_8\text{AsO}, 2\text{HgCl}$ , and which dissolves in boiling water, and again separates from it in crystals on cooling. Bromide of mercury forms an analogous compound.

Oxide of cacodyl dissolves in several acids, with which it appears to play the part of a weak base. By adding nitrate of silver to a solution of oxide of cacodyl in nitric acid a white crystalline precipitate is formed, of which the formula is  $3\text{C}_4\text{H}_8\text{AsO}, (\text{AgO}, \text{NO}_3)$ .

§ 1382. Exposed to the air, oxide of cacodyl becomes heated and incandescent, its combustion being complete, while thick vapours of arsenious acid are formed. But if cacodyl covered with a stratum of water be exposed to the air, the oxygen is slowly absorbed, and arsenious acid, a peculiar ethereal substance, and a more oxygenated product of cacodyl, *cacodylic acid*, are formed. By adding a sufficient quantity of water the cacodylic acid is dissolved; and by evaporating the solution and treating with boiling alcohol, the alcoholic liquor deposits, on cooling, cacodylic acid in colourless crystals. This substance, which is inodorous and nearly tasteless, does not change in the air, and is poisonous, but less so than arsenious acid. It is decomposed at  $446^\circ$  without distilling; its formula is  $\text{C}_4\text{H}_8\text{AsO}_4 + \text{HO}$ ; and it combines with bases without yielding crystallizable salts. Protochloride of tin and phosphorous acid abstract its oxygen and restore it to the state of oxide of cacodyl.

§ 1383. By distilling with highly concentrated chlorohydric acid the compound of oxide of cacodyl with chloride of mercury, a *chloride of cacodyl*  $\text{C}_4\text{H}_8\text{AsCl}$  is obtained, which should be brought into contact with chloride of calcium and quicklime, and then redistilled. Chloride of cacodyl is a colourless liquid, heavier than water, of a sharp smell, and insoluble in water and ether, but soluble in all proportions in alcohol. It resists a temperature of  $-49^\circ$  without becoming solid, and boils at a little above  $212^\circ$ , its vapour becoming incandescent in contact with the air. Nitrate of silver wholly abstracts its chlorine and reproduces oxide of cacodyl. When oxide of cacodyl is treated with gaseous chlorohydric acid, chloride of cacodyl is also formed, but a portion is precipitated in combina-

tion with the water formed. The density of the vapour of chloride of cacodyl is 4.86; and its equivalent corresponds, therefore, to 4 volumes of vapour.

A bromide and iodide of cacodyl may be obtained by similar processes.

Chloride of cacodyl is partially decomposed by contact with water, a combination of 3 equiv. of oxide of cacodyl with 3 equiv. of chloride of cacodyl being formed, which is volatile, and boils at  $228.2^{\circ}$ , the density of its vapour being 5.35, so that it is formed of 3 vol. of vapour of chloride of cacodyl and 1 vol. of oxide of cacodyl without condensation. The bromide and iodide of cacodyl yield similar compounds.

By adding perchloride of platinum to an alcoholic solution of chloride of cacodyl, a brick-red precipitate is obtained, which is, probably, a simple combination of the two substances; while, if the liquid be boiled, the precipitate is redissolved, and yields a liquor from which neither the platinum nor the chloride of cacodyl can be precipitated by reagents which commonly produce that effect. This new compound is a true base which forms crystallizable compounds with several acids.

§ 1384. A *sulphide of cacodyl*  $C_4H_6AsS$  is obtained by distilling chloride of cacodyl with sulfhydrate of sulphide of barium, when sulfhydric acid is disengaged, while water and the sulphide of cacodyl pass over in distillation, the latter of which is purified by digesting it over chloride of calcium and carbonate of lead, and then distilling it in a current of hydrogen. Sulphide of cacodyl is a colourless liquid, which does not fume in the air, is insoluble in water, but readily soluble in alcohol and ether. It combines directly with sulphur and forms a more sulphuretted compound, which may be obtained crystallized by dissolving it in ether. It rapidly absorbs the oxygen of the air, and then forms several compounds, among which cacodylic acid is observed. Chlorohydric acid decomposes sulphide of cacodyl, disengaging sulfhydric acid, while chloride of cacodyl is formed; sulphuric and phosphoric acids also decompose it, a sulphate and phosphate of oxide of cacodyl being formed.

The density of the vapour of sulphide of cacodyl is 8.39, and its formula therefore corresponds to 2 volumes of vapour.

§ 1385. *Cyanide of cacodyl*  $C_4H_6AsCy$  is obtained by distilling oxide of cacodyl with cyanide of mercury, when oxide of mercury remains in the retort, while the cyanide of cacodyl distils over and forms, at the bottom of the water in the receiver, an oily stratum, which, on cooling, assumes a crystalline appearance. The crystals are pressed between several folds of tissue-paper, and distilled over baryta. Cyanide of cacodyl melts at  $90.5^{\circ}$ , boils at  $284^{\circ}$ , and is but slightly soluble in water, but largely so in alcohol and ether.

It is an excessively poisonous substance, the vapour of which it

VOL. II.—2 W

is very dangerous to inhale, and it oxidizes rapidly in the air. The density of its vapour is 4.55, and its equivalent is represented by 4 volumes of vapour.

§ 1386. By heating, protected from the air, cleanly scraped zinc with chloride of cacodyl, the metal is attacked without any evolution of hydrogen, and a white crystalline mass is obtained, on treating which with water to dissolve the chloride of zinc, an oleaginous liquid, heavier than water, separates, which is digested for some time with highly polished zinc, and then distilled after having been allowed to remain for some time over chloride of calcium and quicklime. This substance, which is *cacodyl*, the radical of all the compounds just described, consists of a colourless, highly refracting liquid, still more inflammable than the oxide of cacodyl, which it closely resembles: it solidifies at  $212^{\circ}$ , and boils at about  $338^{\circ}$ . Exposed to a feeble current of air, it forms a thick cloud, and is first converted into oxide of cacodyl, and then into cacodylic acid. Sulphur, chlorine, and bromine combine directly with it, and form sulphide, chloride, and bromide of cacodyl.

The density of its vapour is 7.28, and its equivalent  $C_4H_6As$  corresponds to 2 volumes of vapour.

The products of cacodyl present a double interest, first as organic substances of which arsenic is the chief constituent, and secondly, because they belong to the small number of organic substances in which the existence of a compound radical has been proved, which, when isolated, reproduces, by direct combination, all the substances of the series.

#### PRODUCTS OF THE ACTION OF CHLORINE ON SUBSTANCES OF THE ALCOHOLIC SERIES.

##### *Action of Chlorine on Chlorohydric Ether.*

§ 1387. In a badly lighted situation, chlorine exerts no action on chlorohydric ether; while in a bright light, or still better, in the direct rays of the sun, reaction ensues with development of heat, chlorohydric acid being disengaged, while an ethereal liquid condenses. When any considerable quantity of this liquid is to be prepared, the apparatus is arranged as represented in fig. 680. Into the flask A is introduced alcohol saturated with chlorohydric acid gas, or merely a mixture of equal volumes of alcohol and highly fuming chlorohydric acid of commerce. The gas is passed through a first washing-bottle B containing water, then through a second bottle C with concentrated sulphuric acid, and lastly through a third bottle D again containing water. Into another flask I is introduced peroxide of manganese and chlorohydric acid to generate the chlorine, which is washed in the water in the bottle H. The two gases are conveyed, by two tubes, the orifices of which are opposite to each other, into the flask E, having three tubulures, the

lower of which passes into the bottle F intended to collect the least volatile portion of the product, while the most volatile portion collects in the bottle G, which should be well cooled. The flask E in

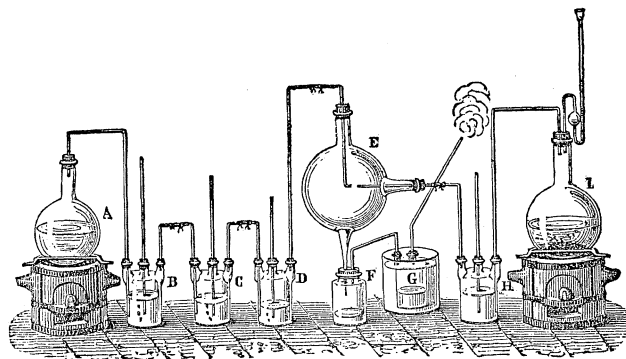


Fig. 680.

which the two gases unite should be exposed to the sun, at least in the commencement of the operation; for when the reaction is once established, it continues in the shade, and does not cease with the setting of the sun. Care must be taken to keep the chlorohydric ether in excess as regards the chlorine, as otherwise the latter would exert a subsequent action on the first product and produce a second one more chlorinated. It is moreover difficult to avoid, in an operation which lasts for a long time, the formation of a small quantity of this product, unless the operation be continued in the shade; but, as it is less volatile, nearly the whole of it remains in the first receiving-bottle. The liquid is washed several times with water, and then distilled in a water-bath, over quicklime, in order to entirely deprive it of water and chlorohydric acid. The first drops which pass over in distillation should be rejected, because they often contain a small quantity of unaltered chlorohydric ether, which remains in solution; and the last fourth is also set aside because it may contain a small proportion of more highly chlorinated products.

The formula of the liquid thus obtained is  $C_4H_4Cl_2$ ; and it is *monochlorinated chlorohydric ether*, presenting the same composition as Dutch liquid, the taste and smell of which it exactly resembles. The density of its vapour is also exactly the same, 3.42; while its boiling point is very different, for monochlorinated chlorohydric ether boils at  $147.2^\circ$ , while Dutch liquid boils at  $180.5^\circ$ . These two substances also differ entirely in their chemical reactions: thus, an alcoholic solution of potassa immediately decomposes Dutch liquid when cold, chloride of potassium being formed and monochlorinated bicarburetted hydrogen  $C_4H_3Cl$  disengaged. Nothing simi-



lar occurs in monochlorinated chlorohydric ether; and if this substance be distilled with an alcoholic solution of potassa, a very small fraction only of it is changed, without producing monochlorinated bicarburetted hydrogen. Dutch liquid is acted on immediately, when cold, by potassium, hydrogen being disengaged, while chloride of potassium and monochlorinated bicarburetted hydrogen are formed; but in monochlorinated chlorohydric ether, on the contrary, the potassium preserves its metallic brilliancy. Dutch liquid differs therefore from its isomeric, monochlorinated chlorohydric ether, in the fact that 1 equivalent of hydrogen and 1 equivalent of chlorine exist in the compound in quite different conditions. In the reactions just described, these two elements behave as if they existed, in Dutch liquid, in the state of chlorohydric acid; for which reason some chemists have assigned to Dutch liquid the formula  $C_4H_3Cl, HCl$ , and to monochlorinated chlorohydric ether the formula  $C_4H_4Cl_2$ , which perfectly represents the difference of the chemical reactions.

§ 1388. By causing chlorine to act gradually and with the assistance of solar light on monochlorinated chlorohydric ether, with the precautions described in the preparation of the various degrees of chlorination of Dutch liquid, the following products are obtained:

Bichlorinated chlorohydric ether .....  $C_4H_3Cl_3$ , isomeric with monochlorinated Dutch liquid;  
 Terchlorinated chlorohydric ether.....  $C_4H_2Cl_4$ , isomeric with bichlorinated Dutch liquid;  
 Quadrichlorinated chlorohydric ether.....  $C_4HCl_5$ , isomeric with terchlorinated Dutch liquid;  
 Perchlorinated chlorohydric ether.....  $C_4Cl_6$ , identical with perchlorinated Dutch liquid, or sesquichloride of carbon.

The final product of the action of chlorine on chlorohydric ether is therefore the same as that afforded by Dutch liquid: it is crystallized sesquichloride of carbon, the properties of which have been described, (§ 1338.) The three products  $C_4H_3Cl_3$ ,  $C_4H_2Cl_4$  and  $C_4HCl_5$ , derived from chlorohydric ether, differ entirely in their physical properties from the isomeric products obtained from Dutch liquid; and, in fact,

Bichlorinated chlorohydric ether.....	$C_4H_3Cl_3$	boils at...	167.0°
Monochlorinated Dutch liquid.....	"	"	239.0°
Terchlorinated chlorohydric ether...	$C_4H_2Cl_4$	"	215.6°
Bichlorinated Dutch liquid.....	"	"	275.0°
Quadrichlorinated chlorohydric ether	$C_4HCl_5$	"	294.8°
Terchlorinated Dutch liquid.....	"	"	307.4°

The last product, the sesquichloride of carbon, which is common to both series, boils at 356°.

The difference between the boiling points of isomeric chlorinated products of chlorohydric ether and Dutch liquid becomes smaller and smaller, as the quantity of chlorine substituted for the hydrogen increases; and lastly, it is reduced to nothing in the perchlorinated products, which are identical: thus

The difference of ebullition between monochlorinated chlorohydric ether and Dutch liquid is.....	71.0°
Between bichlorinated chlorohydric ether, and monochlorinated Dutch liquid, it is.....	72.0°
Between terchlorinated chlorohydric ether and bichlorinated Dutch liquid, it is.....	59.4°
Between quadrichlorinated chlorohydric ether and terchlorinated Dutch liquid, it is.....	12.6°
Lastly, between identical perchlorinated products, it is necessarily .....	0.0°

§ 1389. Bichlorinated and terchlorinated chlorohydric ethers differ very distinctly in their chemical reactions from their isomerics, monochlorinated and bichlorinated Dutch liquid. In fact, the products derived from Dutch liquid yield, with an alcoholic solution of potassa, the former, bichlorinated bicarburetted hydrogen  $C_4H_2Cl_2$ , the latter, terchlorinated bicarburetted hydrogen  $C_4HCl_3$ ; while the isomeric products derived from chlorohydric ether afford no similar results: they resist the action of potassa, and, after a long time, substitutions of oxygen for chlorine alone are formed. The differences exhibited in this chemical reaction by the two isomeric series is therefore perfectly explained by writing the products derived from Dutch liquid  $C_4H_2Cl_2, HCl$  and  $C_4HCl_3, HCl$ .

Quadrichlorinated chlorohydric ether and its isomeric terchlorinated Dutch liquid exhibit also remarkable differences in their chemical reactions; the latter substance being readily acted on by the alcoholic solution of potassa, and yielding perchlorinated bicarburetted hydrogen  $C_4Cl_4$  or chloride of carbon; while quadrichlorinated chlorohydric ether is much more easily acted on by the alcoholic solution of potassa than the products which preceded it, but the reaction is far from being as simple as that exerted on its isomeric.

§ 1390. Chlorohydric ether may be regarded as being derived from a carburetted hydrogen  $C_4H_6$ , which has hitherto not been obtained, and which, in its constitution, would differ from carburetted hydrogen, which we assumed (§1339) as the starting point of the series of Dutch liquid, and we should then have the following series:

Carburetted hydrogen unknown.....	$C_4H_6$ , density “	boils at “
Chlorohydric ether.....	$C_4H_5Cl$ “	0.840 “ 54.5°
Monochlorinated chlorohydric ether.	$C_4H_4Cl_2$ “	1.174 “ 147.2°
Bichlorinated “ “	$C_4HCl_3$ “	1.372 “ 167.0°

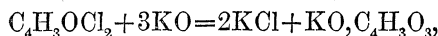
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## Terchlorinated chlorohydric

ether.....	$C_4H_2Cl_4$	density 1.530	boils at $215.6^\circ$
Quadrichlorinated chlo. ether..	$C_4HCl_5$	" 1.644	" $294.8^\circ$
Perchlorinated	" " $C_4Cl_6$	" "	" $356.0^\circ$

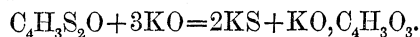
*Products of the Action of Chlorine on Ether  $C_4H_5O$ .*

§ 1391. Ether is very violently acted on by chlorine, the temperature rising considerably, while the substance turns black and ignites, if the chlorine be in too great quantity, and if the apparatus is exposed to the sun. By operating in a darkened room, and exhausting the action of the chlorine by elevating even slightly the temperature toward the close of the operation, a product is obtained which may be regarded as *bichlorinated ether*, for its formula is  $C_4H_3Cl_2O$ . It is a colourless, oleaginous liquid, of a smell resembling fennel; and its density is 2.5, while it decomposes at about  $284^\circ$  without boiling. Heated with an alcoholic solution of potassa, chloride of potassium and acetate of potassa are formed, from the following equation:



the 2 equiv. of chlorine are therefore replaced by 2 equiv. of oxygen.

By heating bichlorinated ether in a current of sulphydric acid gas, chlorohydric acid is disengaged, and, if it be sufficiently heated, an oleaginous liquid, the greater portion of which solidifies on cooling, passes over in distillation. This substance is removed, pressed between several folds of tissue-paper, and dissolved in boiling alcohol. On cooling, crystals of the two substances are separated, which are again crystallized, until only the prismatic forms of a single species are obtained. The composition of the substance then corresponds to the formula  $C_4H_3S_2O$ , and is derived from the primitive substance  $C_4H_3Cl_2O$ , bichlorinated ether, by 2 equiv. of sulphur being substituted for 2 equiv. of chlorine; and it is therefore ether  $C_4H_5O$  of which 2 equiv. of hydrogen have been replaced by 2 equiv. of sulphur, or *bisulphuretted ether*. It is insoluble in water, and decomposed at about  $248^\circ$ , without distilling. An alcoholic solution of potassa decomposes it, forming sulphide of potassium and acetate of potassa:



Alcoholic liquors which have been used in the purification of bisulphuretted ether deposit, after evaporation, yellow aciculæ of the formula  $C_4H_3ClSO$ , which consist of bichlorinated ether, in which a single equivalent of chlorine has been replaced by 1 equiv. of sulphur.

§ 1392. By arresting the action of chlorine on ether at a suitable moment, the liquid contains a large quantity of *monochlorinated ether*  $C_4H_4ClO$ , which is particularly formed when chlorine and

vapour of ether in excess are introduced into a flask exposed to diffused light, and the liquid obtained is distilled, dividing the products into fractions, when the first portions which pass over in distillation contain a large amount of ether and chlorohydric ether, while the monochlorinated ether  $C_4H_4ClO$  does not distil before about  $356^\circ$ . This product is often formed in large quantities in the preparation of Dutch liquid when the bicarburetted hydrogen becomes loaded with vapours of ether.

The preparation of pure chlorinated ethers is often very difficult, and would be almost impossible if carried on in the sun. A large quantity of chlorohydric ether is necessarily formed in this preparation, from the reaction which the chlorohydric acid, arising from the combination of the chlorine with the hydrogen abstracted from the ether, exerts on the unaltered ether  $C_4H_5O$ ; and if the operation be carried on in a darkened place, the chlorohydric ether is disengaged almost entirely, without being ultimately attacked by the chlorine; which would not be the case in the light of the sun, because the chlorohydric ether would then be attacked by the chlorine, and yield chlorinated chlorohydric ethers, much less volatile, and which would remain dissolved in the chlorinated ethers.

§ 1393. The action of chlorine on ether does not stop at bichlorinated ether  $C_4H_3Cl_2O$ , but continues, if the experiment be made in the sun, furnishing liquids richer and richer in chlorine, and correspondingly poor in hydrogen. By exhausting the action of the chlorine, by pouring the highly chlorinated liquid into large bottles filled with dry chlorine, and exposed to intense solar light, there are found white crystals, remarkable for their beautiful forms and their size, consisting of *perchlorinated ether*  $C_4Cl_5O$ , in which all the hydrogen of ether  $C_4H_5O$  has been replaced by chlorine. Perchlorinated ether melts at  $156.2^\circ$ , and, when heated to  $572^\circ$ , it does not boil, but is decomposed into sesquichloride of carbon  $C_4Cl_6$ , and a liquid product of the formula  $C_4Cl_4O_2$ , consisting of *chlorinated aldehyd*. The decomposition is represented by the following equation:



When perchlorinated ether is heated with an alcoholic solution of monosulphide of potassium, chloride of potassium and a new compound of the formula  $C_4Cl_3O$  are found, which substance evidently belongs to the series of bicarburetted hydrogen  $C_4H_4$ ; 3 equiv. of chlorine having replaced 3 of hydrogen, and 1 equiv. of oxygen occupying the place of the last equiv. of hydrogen. Treated with chlorine, in the sun, the substance  $C_4Cl_3O$  reproduces perchlorinated ether  $C_4Cl_5O$ . The two substances  $C_4Cl_5O$  and  $C_4Cl_3O$  present, therefore, relations precisely similar to those existing between the two chlorides of carbon  $C_4Cl_6$  and  $C_4Cl_4$ , the first of which belongs to the series of chlorohydric ether, and the second to that of bicarburetted hydrogen.

It is essential, in order to obtain pure perchlorinated ether, to expose to the action of chlorine in excess, influenced by the solar rays, only ether already completely chlorinated in the shade and freed from ether and chlorohydric ether; as otherwise large quantities of chloride of carbon  $C_4Cl_6$ , which would remain mixed with the chlorided ether, would be inevitably formed.

It is equally necessary to operate upon anhydrous ether, and with perfectly dried chlorine, for, if water be present, it is entirely decomposed by the chlorine, and its nascent oxygen exerts an oxidizing action on the ether, (§ 1366,) forming aldehyd  $C_4H_4O_2$ , and consequently causing the products of the action of chlorine on aldehyd to be mixed with those of the action of chlorine on ether  $C_4H_5O$ .

*Action of Chlorine on Sulfhydic Ether,  $C_4H_5S$ .*

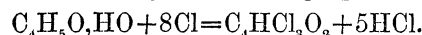
§ 1394. Sulfhydic ether is powerfully acted on by chlorine, with disengagement of chlorohydric acid, and it even ignites when projected into a bottle filled with gaseous chlorine. After attacking the sulfhydic ether by chlorine, in a darkened place, and introducing the chlorine slowly, in order to avoid too great an elevation of temperature, the apparatus is exposed to the sun as soon as the action ceases, and chlorine passed through until chlorohydric acid is no longer disengaged. The liquid is exposed in vacuo near a cup filled with a concentrated solution of caustic potassa, which absorbs the chlorine and chlorohydric acid it contains; and there remains a yellow liquid, of an extremely disagreeable and persistent smell, of the density 1.673, and which decomposes at about  $320^\circ$ . Its formula is  $C_4HClS$ , and it constitutes *quadrichlorinated sulfhydic ether*: intermediate products probably exist, but they have not yet been discovered.

*Action of Chlorine on Alcohol  $C_4H_6O_2$ .*

§ 1395. Chlorine acts very powerfully on alcohol, and yields very various products, according to the strength of the alcohol. We shall suppose the most simple case, that in which the alcohol is anhydrous, and admit that the chlorine is perfectly dry. Alcohol absorbs a large quantity of chlorine, without any disengagement of chlorohydric acid, if its temperature be kept sufficiently low; and if, after a certain length of time, water be poured on the product, an oleaginous liquid is separated from it, which falls to the bottom of the vessel, and is a mixture of several chlorinated substances: this substance is called *chloralcoholic oil*, but the substances composing it are unknown. If the action of chlorine on alcohol be indefinitely continued, an oily liquid soon separates, which gradually increases, and finally constitutes the whole mass. This liquid, which is also very complex, is gently heated; in order to disengage the very volatile products, such as chlorohydric ether and its highly chlorinated products, which, if they remained in the mixture, would

be subsequently transformed into chloride of carbon  $C_4Cl_6$ . The action of the chlorine is continued, the temperature elevated, and it is terminated by the assistance of the solar rays. The liquid obtained should be mixed with 3 or 4 times its volume of sulphuric acid, and the bottle is shaken several times, after which its contents are distilled over sulphuric acid. The product of this distillation is again distilled in a tubulated retort furnished with a thermometer, and the first products, containing a large amount of chlorohydric acid, are rejected, the product distilling at  $201.2^\circ$  being separately collected, which forms a colourless liquid, of a suffocating odour, and exciting to tears. Its density is 1.502, and its composition corresponds to the formula  $C_4HCl_3O_2$ : it is called *chloral*, but is only *terchlorinated aldehyd*. Its equivalent corresponds to 4 volumes of vapour.

The formation of chloral by the action of chlorine on alcohol, is explained in the following manner:—The formula of anhydrous alcohol is  $C_4H_6O_2$ , while, in the majority of its reactions, it behaves like a compound of ether  $C_4H_5O$  and water  $HO$ ; and the action of chlorine on alcohol yields the same products as if it acted on a mixture of 1 equivalent of ether and 1 equivalent of water: it first exerts an oxidizing action, by decomposing the equivalent of water, and the product of this action is aldehyd  $C_4H_4O_2$ , which is in fact obtained in large quantity during the first periods of the action of chlorine on alcohol, and may be separated by distillation. But if the action of the chlorine continues, as there is no more water, the previous oxidizing action is replaced by a chlorinating action, by which the substance loses hydrogen and gains equivalent quantities of chlorine; the reaction ceasing, even in the most intense solar heat of our climate, at the moment when the substance still retains 1 equivalent of hydrogen, and is converted into chloral  $C_4HCl_3O_2$ . The reaction is expressed by the following equation:

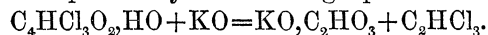


Chloral should therefore be considered as *terchlorinated aldehyd*. It has hitherto been in vain attempted to remove directly by chlorine the equivalent of hydrogen which remains in terchlorinated aldehyd, so as to produce *quadrichlorinated* or *perchlorinated aldehyd*  $C_4Cl_4O_2$ , although this substance has been indirectly obtained, it being one of the products of the decomposition of perchlorinated ether  $C_4Cl_5O$ , by heat, (§ 1393.)

Chloral dissolves largely in water without decomposing, and if the solution be evaporated in vacuo over concentrated sulphuric acid, crystals are formed consisting of a combination of chloral with water, *hydrated chloral*  $C_4HCl_3O_2,HO$ , which exhibits the molecular grouping of alcohol  $C_4H_5O,HO$ . Chloral has so great an affinity for water that it attracts the moisture of the air, and is converted into crystals of hydrated chloral. The crystals may be

sublimed without decomposing, while they give off their water when they are distilled with concentrated sulphuric acid, and allow anhydrous chloral to pass over in distillation.

Chloral is decomposed by an aqueous solution of potassa, two products belonging to the series of protocarburetted hydrogen  $C_2H_4$  being formed, namely, formic acid  $C_2H_3O_3$  and chloroform  $C_2HCl_3$ ; and the reaction is expressed by the following equation:



The molecular grouping of alcohol is therefore doubled in this case, and produces two groups, exhibiting the grouping of protocarburetted hydrogen.

When anhydrous chloral is left for some time in a tube hermetically closed it becomes cloudy, and a white substance, which increases until it has taken the place of the whole of the liquid, is deposited on the sides of the tube. This is an isomeric modification of chloral, which no longer presents any of the characteristic properties of the latter substance: thus it is inodorous, resembles porcelain in appearance, and no longer dissolves in water, whence it has been called *insoluble chloral*. It reproduces, when heated, ordinary

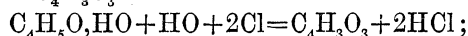


Fig. 681.

chloral, which distils over. If the tube in which the chloral is contained be shaped as represented in fig. 681, the part *a*, in which the chloral is solidified, may be heated, and the liquid chloral obtained in the part *b*; and since the liquid chloral soon solidifies again, the experiment may be indefinitely repeated in the same tube.

It is important to remark that liquid chloral  $C_4HCl_3O_2$  does not correspond exactly to aldehyd, for its equivalent is represented by 4 volumes of vapour, while that of aldehyd  $C_4H_4O_2$  is represented by 2 volumes. It must therefore be admitted that in the conversion of aldehyd into terchlorinated aldehyd or chloral, each molecule of aldehyd has afforded 2 molecules of chloral, or rather that the molecules, by being charged with chlorine, have separated so as to fill a double space. If the first hypothesis is correct, insoluble chloral may possibly present the molecular grouping of aldehyd; while insoluble chloral may possibly also correspond to one of the isomeric modifications of aldehyd described § 1367—to elaldehyd or metaldehyd.

If the alcohol contained water, or if the chlorine were not perfectly dry, the reaction might be still more complicated. Supposing the alcohol to contain an equivalent of water, the first stage of oxidation due to the decomposition of the water would not stop at the formation of aldehyd  $C_4H_4O_2$ , but would convert this substance into acetic acid  $C_4H_3O_3$ .



and at a later period during the stage of chlorination, products of the action of chlorine on acetic acid would be formed.

But again, acetic acid, by dissolving in unaltered alcohol, might produce, particularly under the influence of the chlorohydric acid, which is copiously formed, acetic ether, which at a later period would form, by the action of chlorine, chlorinated acetic ether. It will hence be seen how complicated these products may become, and it would be often impossible to disentangle the reactions, unless guided by theory.

Lastly, if the alcohol were very hydrated, the oxidizing stage would continue until the alcohol was wholly converted into water and carbonic acid.

*Products of the Action of Chlorine on Aldehyde  $C_4H_4O_2$ .*

§ 1396. From what has been just said concerning the action of chlorine on alcohol, there remains but little to add touching the action of chlorine on aldehyde. By causing chlorine to act on aldehyde  $C_4H_4O_2$ , a large quantity of chloral  $C_4HCl_3O_2$  is obtained, which is mixed with other less volatile products, which have not yet been examined. They are probably the chlorinated aldehydes  $C_4H_3ClO_2$  and  $C_4H_2Cl_2O_2$ , which a more prolonged action of the chlorine would have converted into chloral.

*Products of the Action of Chlorine on Acetic Acid,  $C_4H_3O_3, HO$ .*

§ 1397. Chlorine acts powerfully on monohydrated acetic acid, and at last, when assisted by the rays of the sun, deprives it wholly of its oxygen, which is replaced by an equivalent quantity of chlorine; a crystallized product  $C_4Cl_3O_3, HO$ , or *chloracetic acid*, which is powerfully acid, and possesses the same capacity of saturation as acetic acid, being formed. Intermediate chlorinated compounds probably exist, but they have not yet been examined. In order to prepare chloracetic acid, ground-stoppered bottles, holding 5 or 6 litres, are filled with very dry chlorine, and into each is poured 4 or 5 grammes of monohydrated acetic acid, after which the bottles are exposed to the sun; when their sides soon become covered with crystals, which consist of a mixture of oxalic and chloracetic acid, while the gas in the bottle is formed of chlorohydric acid and chlorocarbonic gas, resulting from a more advanced decomposition, which takes place, perhaps, in consequence of the small quantity of water from which it is difficult to free the chlorine and the sides of the flask. The crystals being dissolved in water, and the solution evaporated in vacuo over concentrated sulphuric acid, the oxalic acid crystallizes first, when the mother liquid is decanted, completely evaporated, and the residue distilled with anhydrous phosphoric acid. The oxalic acid which might remain is decomposed into oxide of carbon and carbonic acid, and the chloracetic acid distils over, but the first product should not be collected, because it may contain a small proportion of acetic acid.



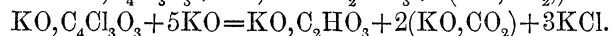
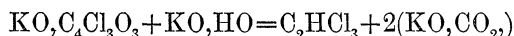
Chloracetic acid crystallizes in rhombohedral lamellæ or in colourless aciculæ, deliquescent in the air; and it melts at  $113^{\circ}$  and boils at about  $392^{\circ}$ . It combines with bases and forms a large number of soluble and crystallizable salts.

The formula of chloracetate of potassa is  $\text{KO}, \text{C}_4\text{Cl}_3\text{O}_3 + 2\text{HO}$ .

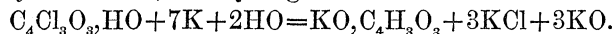
“ of chloracetate of ammonia,  $(\text{NH}_3, \text{HO}), \text{C}_4\text{Cl}_3\text{O}_3 + 4\text{HO}$ .

“ of chloracetate of silver,  $\text{AgO}, \text{C}_4\text{Cl}_3\text{O}_3$ .

The chloracetates heated with an excess of potassa yield chloroform and an alkaline carbonate; and if the action be prolonged, the chloroform is itself converted into formic acid. We have, in fact,



When chloracetic acid is treated with an amalgam formed of 1 part of potassium and 150 parts of mercury, it is converted into ordinary acetic acid, and hydrogen is substituted for the chlorine:

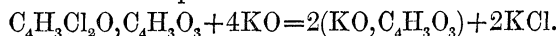


§ 1398. Chloracetic acid forms a compound ether, *chloracetic ether*  $\text{C}_4\text{H}_5\text{O}, \text{C}_4\text{Cl}_3\text{O}_3$ , and a *perchlorinated chloracetic ether*  $\text{C}_4\text{Cl}_5\text{O}, \text{C}_4\text{Cl}_3\text{O}_3$ . Chloracetic ether is prepared by distilling chloracetic acid, or a chloracetate, with a mixture of alcohol and sulphuric acid, and diluting the distilled product with water, when the ether separates in the form of oil. By exposing it to the sun in bottles filled with dry chlorine, it is converted into an oleaginous product, *perchlorinated chloracetic ether*, which boils at  $473^{\circ}$ .

#### *Action of Chlorine on Compound Ethers.*

§ 1399. Chlorine acts on the compound ethers and removes their hydrogen; the hydrogen removed being, in all cases, replaced by an equivalent quantity of chlorine.

The first action of chlorine on acetic ether  $\text{C}_4\text{H}_5\text{O}, \text{C}_4\text{H}_3\text{O}_3$  consists in removing 2 equiv. of hydrogen from simple ether  $\text{C}_4\text{H}_5\text{O}$ , and replacing them by 2 equiv. of chlorine; which furnishes a *bichlorinated acetic ether* of the formula  $\text{C}_4\text{H}_3\text{Cl}_2\text{O}, \text{C}_4\text{H}_3\text{O}_3$ . It is decomposed by an alcoholic solution of potassa, and yields of acetate of potassa and chloride of potassium



If, on the contrary, the action of the chlorine be exhausted by intense solar radiation, perchlorinated chloracetic ether results,  $\text{C}_4\text{Cl}_5\text{O}, \text{C}_4\text{Cl}_3\text{O}_3$ .

By passing chlorine, under the influence of the solar rays, into oxalic ether  $\text{C}_4\text{H}_5\text{O}, \text{C}_2\text{O}_3$ , until chlorohydric acid is no longer disengaged, the ether is converted into a crystalline mass, which may be purified by pressing it between tissue-paper. This is *perchlorinated oxalic ether*  $\text{C}_4\text{Cl}_5\text{O}, \text{C}_2\text{O}_3$ , which melts at  $291.2^{\circ}$ , and is decomposed at a higher temperature.

Carbonic ether  $C_4H_5O, CO_2$  subjected to the action of chlorine in diffused light yields chlorinated ether  $C_4H_3Cl_2O, CO_2$ ; and if the action of the chlorine be continued under the influence of the direct rays of the sun, perchlorinated carbonic ether  $C_4Cl_5O, CO_2$  is obtained.

§ 1400. By comparing together the numerous compounds derived from alcohol, it will be observed that the greater part of them are formed by means of the molecule of ether  $C_4H_5O$ , or that of alcohol  $C_4H_5O, HO$ , in which the hydrogen or oxygen is replaced by equivalent quantities of other elements: oxygen, sulphur, chlorine, etc. When the hydrogen is replaced by equivalent quantities of chlorine, the equivalent of the derived substance is, *in general*, represented by the same number of volumes of vapour as the substance from which it is derived, as in the chlorinated products derived from chlorohydric ether. The same is true when oxygen is replaced by sulphur, as in ether  $C_4H_5O$  and sulfhydric ether  $C_4H_5S$ . In these different cases the gaseous volume of the element substituted is the same as that of which it takes the place. But when oxygen, the equivalent of which is 1 vol., is replaced by chlorine, of which the equivalent is 2 vol., the equivalent in volume of the substance derived is often different from that of the original substance: thus, the equivalent of ether  $C_4H_5O$  is 2 vol., while that of chlorohydric ether is 4 vol. Many exceptions to these rules nevertheless occur: thus, aldehyde is derived from ether by the replacement of 1 equiv. of hydrogen (2 vol.) by 1 equiv. of oxygen, (1 vol.), and yet aldehyde  $C_4H_4O_2$  is represented by 2 vol. of vapour, like ether  $C_4H_5O$ ; while by replacing 3 equiv. of hydrogen (6 vol.) by 3 equiv. of chlorine (6 vol.) in the molecule of aldehyde, chloral or terchlorinated aldehyde is obtained, of which the equivalent  $C_4HCl_3O_2$  is represented by 4 vol., while that of aldehyde is represented by 2 vol.

When chlorine is substituted for hydrogen, the chemical properties of the compound, as regards its acid, basic, or neutral reactions, do not, in general, appear to be changed; the most striking example of which is given by chloracetic acid, which is an acid as powerful as acetic, and possesses exactly the same capacity of saturation. The compound chlorinated ethers present additional examples, and others shall subsequently be described which are not less remarkable. But when hydrogen is replaced by oxygen, the basic, acid, or neutral properties of the substances change wonderfully. Thus ether  $C_4H_5O$ , which has a manifest affinity for acids, loses this property when it is converted into aldehyde  $C_4H_4O_2$ , and becomes a powerful acid when changed into acetic acid  $C_4H_3O_3$ .

In order to appreciate more readily the relations of composition of the substances belonging to the alcoholic or vinic series, we have collected them in the following table:

VOL. II.—2 X

TABLE OF THE COMPOUNDS DERIVED FROM ETHER,  $C_4H_6O$ , OR  
FROM ALCOHOL,  $C_4H_6O, HO$ , BY MEANS OF SUBSTITUTION.

Carburetted hydrogen unknown  $C_4H_6$ , which may be regarded as the starting point of the whole series.

SIMPLE ETHERS.

Ether.....	$C_4H_6O$	2 vol. of vapour.
Sulphydic ether.....	$C_4H_6S$	2 “ “
Hydroselenic “ .....	$C_4H_6Se$	“ “ “
Hydrotelluric “ .....	$C_4H_6Te$	“ “ “
Chlorohydric “ .....	$C_4H_6Cl$	4 “ “
Bromohydric “ .....	$C_4H_6Br$	4 “ “
Iodohydric “ .....	$C_4H_6I$	4 “ “
Cyanohydric “ .....	$C_4H_6Cy$	4 “ “
Sulphocyanhydric ether.....	$C_4H_6SCy$	4 “ “

COMPOUND ETHERS.

*Alcohols.*

Ordinary alcohol.....	$C_4H_6O, HO$	4 vol. of vapour.
Sulphydic “ .....	$C_4H_6S, HS$	4 “ “
Sulphopotassic alcohol.....	$C_4H_6S, KS$	
Sulphoplumbic “ .....	$C_4H_6S, PbS$	
Sulphomercuric “ .....	$C_4H_6S, Hg_2S$	

*Compound Ethers properly so called.*

General formula ( $\bar{A}$ representing the acid).....	$C_4H_6O, \bar{A}$	2 or 4 vol.
Boracic ether.....	$C_4H_6O, 2BO_3$	
1st Silicic ether.....	$3C_4H_6O, SiO_3$	
2d Silicic ether.....	$3C_4H_6O, 2SiO_3$	

*Vinic acids.*

General formula of vinic acids formed by the monobasic acids $\bar{A}$ .....	$(C_4H_6O + HO), 2\bar{A}$
Formula of vinic acids produced by the tribasic acids, such as $PO_3, 3HO$ .....	$(C_4H_6O + 2HO), PO_3$

PRODUCTS SUCCESSIVELY DERIVED FROM ETHER  $C_4H_6O$ .

*1st. By oxidation.*

Ether.....	$C_4H_6O$	2 vol.
Acetal.....	$(2C_4H_6O, C_4H_6O_2)$	
Aldehyde.....	$C_4H_6O_2$	2 “
Anhydrous acetic acid.....	$C_4H_6O_3$	unknown,
remains in combination with the water formed, and yields		
Hydrated acetic acid.....	$C_4H_6O_3, HO$	4 vol.
but corresponding to alcohol.....	$C_4H_6O, HO$	

*2dly. By the action of Chlorine.*

Ether.....	$C_4H_6$	O
Monochlorinated ether.....	$C_4H_5Cl$	O
Bichlorinated ether.....	$C_4H_4Cl_2$	O
.....		
Perchlorinated ether.....	$C_4Cl_4$	O.

3dly. *By the successive action of Chlorine and Sulphur.*

Monochlorinated and monosulphuretted ether.....	$C_4H_3ClSO$
Bisulphuretted ether.....	$C_4H_3S_2O$ .

PRODUCTS DERIVED FROM SULFHYDRIC ETHER  $C_4H_3S$ .

*By the action of Chlorine.*

Sulphydic ether.....	$C_4H_3S$
.....	.....
Quadrichlorinated sulphydic ether.....	$C_4HCl_4S$ .

PRODUCTS DERIVED FROM CHLOROHYDRIC ETHER,  $C_4H_3Cl$ .

*By the action of Chlorine.*

Chlorohydric ether.....	$C_4H_3Cl$	4 vol.
Monochlorinated chlorohydric ether.....	$C_4H_4Cl_2$	4 "
Bichlorinated " " .....	$C_4H_3Cl_3$	4 "
Terchlorinated " " .....	$C_4H_2Cl_4$	4 "
Quadrichlorinated " " .....	$C_4HCl_5$	4 "
Perchlorinated " " .....	$C_4Cl_6$	4 "

PRODUCTS DERIVED FROM ALDEHYDE  $C_4H_4O_2$ .

1st. *By the action of Oxygen.*

Aldehyde.....	$C_4H_4O_2$
Acetic acid.....	$C_4H_3O_3$

which remains in combination with the water formed.

2dly. *By the action of Chlorine.*

Aldehyde.....	$C_4H_4O_2$	2 vol.
.....	.....	.....
Terchlorinated aldehyde or chloral.....	$C_4HCl_3O_2$	4 "
Perchlorinated aldehyde.....	$C_4Cl_4O_2$ .	

PRODUCTS DERIVED FROM ALCOHOL  $C_4H_5O, HO$ .

1st. *By the action of Oxygen.*

Alcohol.....	$C_4H_5O, HO$	4 vol.
Aldehyde.....	$C_4H_4O_2$	2 "

parts with its equivalent of water, and belongs to the series of ether.

2dly. *By the action of Chlorine.*

Alcohol.....	$C_4H_5O, HO$	4 vol.
Aldehyde (1st stage of oxidation).....	$C_4H_4O_2$	2 "
Chloral (2d stage of chlorination).....	$C_4HCl_3O_2$	2 "

Aqueous ether  $C_4H_5O + HO$  yields the same products.

PRODUCTS DERIVED FROM AQUEOUS ALCOHOL,  $C_4H_5O, HO + HO$ .

*By the action of Chlorine.*

By an oxidizing action, acetic acid.....	$C_4H_3O_3, HO$ .
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Aqueous ether  $C_4H_5O + 2HO$  yields the same product.

PRODUCTS DERIVED FROM ACETIC ACID  $C_4H_3O_3, HO$ .

*By the action of Chlorine.*

Acetic acid.....	$C_4H_3O_3, HO$	4 vol.
.....	.....	.....
Chloracetic acid.....	$C_4Cl_3O_3, HO$	4 "

## PRODUCTS DERIVED FROM COMPOUND ETHERS.

*By the action of Chlorine.*

On Carbonic ether.....	$C_4H_5O, CO_2$
Bichlorinated carbonic ether.....	$C_4H_3Cl_2O, CO_2$
Perchlorinated carbonic ether.....	$C_4Cl_5O, CO_2$
On Oxalic ether.....	$C_4H_5O, C_2O_3$
Perchlorinated oxalic ether.....	$C_4Cl_5O, C_2O_3$
On Acetic ether.....	$C_4H_5O, C_2H_3O_3$
Bichlorinated acetic ether.....	$C_4H_3Cl_2O, C_2H_3O_3$
Chloroacetic ether.....	$C_4H_5O, C_2Cl_3O_3$
Perchlorinated chloroacetic ether.....	$C_4Cl_5O, C_2Cl_3O_3$

§ 1401. Some chemists regard ether as a hydrate of bicarburetted hydrogen, and give it the formula  $C_4H_4, HO$ ; in which case alcohol becomes a bihydrate of bicarburetted hydrogen, and all the products of the vinic series are considered as derived from the same radical, bicarburetted hydrogen  $C_4H_4$ . In this point of view, chlorohydric ether is a chlorohydrate of bicarburetted hydrogen  $C_4H_4, HCl$ , and should be the first of the series of Dutch liquid  $C_4H_3Cl, HCl$  (§ 1338); and the action of chlorine upon chlorohydric ether should therefore yield products identical with those composing this series. Now we have seen that the products derived from chlorohydric ether exhibit, in fact, the same composition as those derived from Dutch liquid, but that they differ essentially in their properties; and it is therefore evident that ether cannot be regarded as a hydrate of olefiant gas.

Other chemists consider ether  $C_4H_5O$  as an oxide of carburetted hydrogen  $C_4H_5$ , to which they have given the name of *ethyl*, and have supposed it to be the radical of the ethers. All attempts to obtain this hypothetical root in an isolated form, have hitherto failed; and its supposition being entirely gratuitous, does not assist the explanation of chemical reactions.\*

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\* The theory adopted by the author, in which the unknown carburetted hydrogen  $C_4H_5$  is assumed as the starting point of the ether or alcohol series, is entirely French, and is in other countries regarded in a similar manner as the author regards the theory which assumes the hydrocarbon *ethyl*,  $C_4H_5$ , as the radical of which ether is the oxide; but since the masterly investigations of Prof. Frankland, who actually succeeded in isolating ethyl, probability inclines very much to the side of the ethyl theory, which requires description in a work like the present.

Before treating particularly of ethyl one general feature of the theory, which equally applies to a number of other substances, must be described: the theory of the *pairing* or conjugation of organic compounds. An organic body is said to be paired with another when the latter, termed the *pairing* or *conjugate*, enters into combination with the former without the former losing its essential properties; examples of which also occur in inorganic chemistry, when *e. g.* oxide of platinum combines with ammonia to form a new oxide, the *compound oxide of platinum and ammonia*, described (§ 1178,) the salts of which present the same general character with those of oxide of platinum. The formula of the compound oxide is  $PtO, N_3H_6$ , or  $PtO, 2NH_3$ , and it may be regarded as the oxide of a new base, consisting of  $PtN_2H_6$  or  $Pt, 2NH_3$ , 1 equiv. of platinum being paired with

## LACTIC AND BUTYRIC FERMENTATION.

§ 1402. Under certain conditions, and when assisted by ferments, sugars and their congeners experience decompositions very different from those which take place in alcoholic fermentation; and they then give rise to peculiar acids, called *lactic* and *butyric*, and to other substances, the nature of which is but little known. The concomitant circumstances, or those which produce *lactic* and *butyric fermentations*, are still less known than those of the alcoholic fermentation.

The various kinds of sugar, dextrin, sugar of milk, yield a large

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2 equiv. of ammonia; in which case the formula of the oxide in order to express the phenomenon of *pairing*, would be written  $\text{Pt}(\text{N}_3\text{H}_8)\text{O}$  or  $\text{Pt}(2\text{NH}_3)\text{O}$ .

In organic chemistry the pairing of combinations is of frequent occurrence; and one of the most beautiful instances of it is the pairing of hydrogen with one or more equivalents of bicarburetted hydrogen or olefiant gas. Hydrogen may, for the moment, be regarded as a radical, or a metal, of which water is the oxide, sulphydric acid the sulphide, chlorohydric acid the chloride, etc.; and now, by pairing it with 1 equiv. of olefiant gas, (assumed to be  $\text{C}_2\text{H}_2$ ) there results the compound  $\text{H}(\text{C}_2\text{H}_2)$  or  $\text{C}_2\text{H}_3$ ; which, if the theory be correct, ought to form compounds with oxygen, sulphur, chlorine, etc. corresponding to the compounds of those elements with hydrogen. This is actually found to be the case, as will be seen in the description of the substance  $\text{C}_3\text{H}_3$ , or *methyl*, the radical of its oxide *methy*, of which *methylic alcohol*, or *wood-spirit*, is the hydrate, (§ 1406.)

Hydrogen paired with 2 equivalents of olefiant gas, forms the compound  $\text{H}(\text{C}_4\text{H}_4)$ , or  $\text{C}_4\text{H}_5$ , which is the formula of ethyl, and forms an oxide  $\text{H}(\text{C}_4\text{H}_4)\text{O}$ , or ether, corresponding to water, of which alcohol is the hydrate. Ethyl,  $\text{C}_4\text{H}_5$ , is an organic radical, corresponding to a metal in inorganic chemistry, because it has its oxide  $\text{C}_4\text{H}_5\text{O}$ , its chloride  $\text{C}_4\text{H}_5\text{Cl}$ , its sulphide  $\text{C}_4\text{H}_5\text{S}$ , and similar compounds with other metalloids, and because its oxide, ether, forms salts with acids corresponding to those of a metallic base  $\text{RO}$ . Chloride of ethyl, which the author calls chlorohydric ether, undergoes mutual decomposition with hydrate of potassa, forming chloride of potassium and hydrated oxide of ethyl, or alcohol; which behaviour is peculiar to the metals. If the radical be really hydrogen paired with 2 equivalents of olefiant gas, then will the behaviour of ethyl be in all respects analogous to that of hydrogen; and its chloride, sulphide, etc., will have the properties of acids corresponding to chlorohydric, sulphydric, etc.; which is, in fact, the case, as chloride of ethyl forms double chlorides with many metallic chlorides, the formulæ of which may be written  $\text{RCl}, \text{H}(\text{C}_4\text{H}_4)\text{Cl}$ ; and the mercaptids, the general formula of which is  $\text{RS}, \text{H}(\text{C}_4\text{H}_4)\text{S}$ , are instances of double sulphides. Nor does the analogy of hydrogen with its paired compounds stop here; for as hydrogen forms compounds with arsenic, antimony, and phosphorus, so it is probable that methyl  $\text{H}(\text{C}_2\text{H}_2)$  and ethyl  $\text{H}(\text{C}_4\text{H}_4)$  will form similar substances; and Frankland has actually succeeded in forming several of them. Cacodyl, which has been described (§ 1381) is arseniuretted methyl, corresponding to arseniuretted hydrogen, and even possessing its properties; a phosphuretted methyl has been obtained, similar to phosphuretted hydrogen; and combinations of both ethyl and methyl with zinc, according to the formulæ  $\text{H}(\text{C}_4\text{H}_4)\text{Zn}$  and  $\text{H}(\text{C}_2\text{H}_2)\text{Zn}$ , are already discovered; the corresponding compound of hydrogen, however, being yet unknown, which would take the formula  $\text{HZn}$ .

If hydrogen be paired with more than 2 equivalents of olefiant gas, other radicals are formed, which shall be duly mentioned in their proper places; they are *butyryl*, *valyl*, *amyl*, and several others, corresponding to the formula  $\text{H}(\text{C}_6\text{H}_6)$ ,  $\text{H}(\text{C}_8\text{H}_8)$ ,  $\text{H}(\text{C}_{10}\text{H}_{10})$ , etc.

Hydrogen, and all radicals formed by its pairing with olefiant gas, will again form a paired compound with oxalic acid  $\text{C}_2\text{O}_3$ , constituting a series of acids,

2 x 2

amount of lactic acid when they are mixed with a solution of diastase, which has been exposed to the air for some time. Sprouted barley, which has been well soaked in water, is left in the air for two or three days, and then bruised, and, after having diluted it with water it is subjected for several days to a temperature of  $77^{\circ}$

which will be described in the text. It will suffice at present to give a tabular view of the series, since only one of these acids, the acetic, has been already described in the present work.

Hydrogen..	H	paired with	$C_2O_3$	forms <i>formic acid</i> ...	$C_2HO_3$	or	H ( $C_2O_3$ )
Methyl.....	$C_2H_3$	" "	$C_2O_3$	" <i>acetic acid</i> .....	$C_4H_3O_3$	or	$C_2H_3(C_2O_3)$
Ethyl.....	$C_4H_5$	" "	$C_2O_3$	" <i>metacetic acid</i> $C_6H_5O_3$	or	$C_4H_5(C_2O_3)$	
Butyryl....	$C_6H_7$	" "	$C_2O_3$	" <i>butyric acid</i> ....	$C_8H_7O_3$	or	$C_6H_7(C_2O_3)$
Valyl.....	$C_8H_9$	" "	$C_2O_3$	" <i>valeric acid</i> ....	$C_{10}H_9O_3$	or	$C_8H_9(C_2O_3)$
Amyl.....	$C_{10}H_{11}$	" "	$C_2O_3$	" <i>caproic acid</i> ...	$C_{12}H_{11}O_3$	or	$C_{10}H_{11}(C_2O_3)$
Margaryl..	$C_{32}H_{33}$	" "	$C_2O_3$	" <i>margaric acid</i>	$C_{34}H_{33}O_3$	or	$C_{32}H_{33}(C_2O_3)$

The series is nearly complete, and it is probable that the connecting links, up to margaryl, will be discovered ere long.

In the foregoing I have endeavoured to present a general view of the theory adopted in Germany and England, in relation to organic radicals, and paired compounds, without entering into details; and it now remains only to describe the substances which have been discovered since the original was written, and which will be noticed under the chapters where the new compound ought to find its place.

#### *Ethyl* $C_4H_5$ .

This, for a long time hypothetical radical, is obtained isolated by decomposing iodohydric ether,  $C_4H_5I$ , more properly called iodide of ethyl, by means of metallic zinc, in an hermetically sealed tube which has been freed from oxygen by exhaustion with an air-pump. The tube contains, after being heated to above  $300^{\circ}$ , ethyl  $C_4H_5$ , olefiant gas  $C_2H_2$ , and methyl  $C_2H_3$ , formed by the decomposition of a certain quantity of ethyl, besides iodide of zinc, which with the methyl forms methylide of zinc  $C_2H_3Zn$ . The gaseous ethyl, and the olefiant gas are brought into a glass-tube over mercury, and after absorbing the carburetted hydrogen by fuming sulphuric acid, the tube contains pure ethyl, as a colourless and inodorous gas, burning with a brilliant white flame, and condensing at  $9.4^{\circ}$  to a very mobile fluid. The density of the gas being 2.000, its formula  $C_4H_5$  corresponds to 2 volumes.

#### *Stibethyl* $SbC_{12}H_{13}$ .

By moistening with iodohydric ether, in a small flask, a mixture of antimonuret of potassium with quartzose sand, and distilling as soon as iodohydric ether no longer evaporates, the receiver is found to contain *stibethyl*, a compound of antimony with 3 equivalents of ethyl, corresponding to antimoniuiretted hydrogen  $SbH_3$ , and the formula of which is  $SbC_{12}H_{13}$ , or rather  $Sb,3H(C_4H_5)$ . *Stibethyl*, is a very mobile and highly refracting fluid of a disagreeable alliaceous odour, of the density 1.324, boiling at  $317.3^{\circ}$ , and yielding a vapour of the density of 7.440, so that its equivalent corresponds to 4 volumes. It is soluble in alcohol and ether, and a drop of the solution ignites in the air.

A compound  $Sb,H(C_4H_5)$  has also been obtained.

#### *Bismethyl* $BiC_{12}H_{13}$ .

It is obtained with bismuth-potassium similarly as stibethyl is formed with an-

or 86°. The starch of the barley is first converted into glucose by the diastase, after which lactic fermentation is developed by the influence of the air, and the liquid becomes very acid by the quantity of lactic acid formed, which is then saturated with lime, evaporated to the consistence of syrup, and treated with boiling alcohol, which dissolves the lactate of lime.

Lactic acid is still more easily obtained by means of milk, which contains at the same time, the fermenting substance, *sugar of milk*, and an albuminoid matter, *casein*, which acts as a ferment, or generates it. When it is allowed to sour in the air, or *to turn*, a coagulum, which is a combination of lactic acid with casein, is formed; and if bicarbonate of soda be added to neutralize the acid, lactate of soda is formed, while the casein, thus set free, again acts as a ferment on the sugar of milk, and converts an additional quantity of it into lactic acid. A new coagulum of lactate of casein is thus formed, which is also decomposed by bicarbonate of soda; and the process is continued until no caseous precipitate of lactate of casein is formed, that is, until the sugar of milk is wholly decomposed. At the close of the operation, acetic acid is poured into the liquor, which is then boiled, when the casein is wholly precipitated in the form of acetate of casein. The filtered liquor is evaporated to dryness and the residue treated with boiling alcohol, which dissolves the lactate of soda. Instead of the sugar of milk, glucose or even cane-sugar may be added, but the lactic fermentation of the latter kind of sugar is very slow, and in order that it may take place, the cane-sugar must, probably, be previously converted into fruit-sugar, which transformation is very slow, because it is essential to lactic fermentation that the liquid should not contain much acid.

Other albuminoid substances may be substituted for casein: the presence of fatty substances appears to assist the formation of lactic acid, and some chemists even suppose it to be essential.

The formula of lactic acid being  $C_6H_5O_5 + HO$ , 2 equivalents of the acid, therefore contain all the elements of an equivalent of fruit-sugar  $C_{12}H_{12}O_{12}$ ; whence it may be admitted that, in lactic fermentation, the molecules of sugar merely change their grouping, without the intervention of any new elements in the reaction.

§ 1403. When liquors which have undergone lactic fermentation,

timoniuret of potassium, and behaves analogous to stibethyl, from which it differs essentially by decomposing at a certain temperature with a powerful explosion. It is a mobile fluid of the density 1.82, and a highly disagreeable odour; in the air it throws out thick fumes, inflames with a slight explosion and diffuses a deep-yellow smoke of oxyd of bismuth. Composition,  $Bi, 3H(C_4H_4)$ .

*Zinckethyl*  $ZnC_4H_4$ .

It is formed in the decomposition of iodohydric ether, or iodide of ethyl by zinc, and its formula is  $Zn, H(C_4H_4)$ . In contact with the air it burns with a brilliant flame, giving off dense fumes of oxide of zinc.—*W. L. F.*



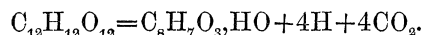
are left to themselves for a longer time, another fermentation is developed, and a new acid, called *butyric* is formed.

Introduce into a large bottle

1. A solution of glucose, marking 8 or 10° of Baumé.
2. A quantity of chalk equal to one-half of the sugar used.
3. A quantity of casein representing, in the dry state, 8 or 10 per cent. of the weight of sugar contained in the solution, for which purpose either cream-cheese, or Brie-cheese is used; freshly prepared gluten may also be substituted for the casein.

The sugar is first transformed into a viscous substance which has hitherto been but little studied, and then into lactic acid, large quantities of which may be obtained by arresting the operation at the proper moment; while if it be continued longer, the lactic acid is finally converted into butyric acid, and a mixture of hydrogen and carbonic acid is disengaged. The butyric fermentation is not generally completed until 2 or 3 months, after which the liquid contains a mixture of butyrate, lactate, and acetate of lime.

The formula of butyric acid being  $C_4H_7O_2$ , we have



which equation accounts for the evolution of hydrogen and carbonic acid during the butyric fermentation.

In order to prepare large quantities of lactic and butyric acid, 3 killog. of sugar are dissolved in 13 killog. of boiling water, to which 15 gm. of tartaric acid have been added, then rotten cheese is added, diluted in sour milk, and 1500 gm. of powdered chalk, the whole is exposed to a temperature of 86° to 95°, and the mass, being shaken from time to time, becomes completely solid in 8 or 10 days. It is then boiled for half an hour with 10 litres of water containing 10 gm. of quick-lime, and after filtering the liquid and evaporating it to the consistence of syrup, it is allowed to crystallize. The crystals of lactate of lime being redissolved in  $2\frac{1}{2}$  times their weight of boiling water, 100 gm. of sulphuric acid diluted with its weight of water, are added, in order to precipitate the lime in the state of sulphate, and isolate the lactic acid; after which the acid liquor, when filtered, is boiled with carbonate of zinc, which forms sulphate and lactate of zinc, a portion of which latter salt separates in crystalline crusts during the cooling of the liquid, while an additional portion is removed by again concentrating it. The lactate of zinc, purified by a second crystallization, is subjected to the action of sulphuric acid gas, and yields pure lactic acid.

The compact mass which has yielded lactic acid, being again left to itself, at a temperature of 98°, becomes liquid and disengages gas; and in 5 or 6 weeks, the new fermentation is terminated. The liquid is then diluted with its weight of water, and a solution of 4 killog. of carbonate of soda is added, which precipitates the lime in the state of carbonate and forms butyrate of soda. The liquor,

when filtered, is evaporated until it occupies only a volume of 4 or 5 litres, when 3 kilog. of sulphuric acid diluted with its volume of water are added. The liquid then separates into two layers, the upper one of which, consisting of butyric acid, is removed and brought into contact with chloride of calcium, and distilled. A single operation may yield as much as 1 kilog. of pure butyric acid.

*Lactic Acid*  $C_6H_5O_5,HO$ .

§ 1404. Lactic acid, concentrated as much as possible, in vacuo, over sulphuric acid, is a colourless liquid, of a density of 1.22, and soluble in all proportions in water and alcohol. Its composition is represented by the formula  $C_6H_5O_5,HO$ , the equivalent of water being capable of being replaced by 1 equiv. of base; and when subjected to heat it gives off its equivalent of water at about  $266^\circ$ , and is changed into anhydrous lactic acid,  $C_6H_5O_5$ , which is solid, fusible, very slightly soluble in water, but dissolving readily in alcohol and ether. In contact with water or moist air, it passes slowly into the state of hydrated lactic acid. Anhydrous lactic acid combines with ammoniacal gas, and yields a product of which the formula is  $NH_3,C_6H_5O_5$ .

When heated to  $482^\circ$  lactic acid is further decomposed; and together with other products, a white crystalline substance of the formula  $C_6H_4O_4$ , is formed, which melts at  $224.6^\circ$ , and sublimes without change at about  $482^\circ$ . It combines with ammoniacal gas and forms a compound  $NH_3,C_6H_4O_4$  *lactamid*, which dissolves without change in water and alcohol. The substance  $C_6H_4O_4$ , which has been improperly called *anhydrous lactic acid*, combines readily with water and reproduces hydrated lactic acid.\*

The lactates of potassa, soda, and ammonia, are deliquescent, and crystallize with difficulty.

Lactate of lime crystallizes in small radiating aciculæ of the formula  $CaO,C_6H_5O_5+5HO$ , and loses its 5 equiv. of water in vacuo, or at a temperature of  $212^\circ$ .

Lactate of zinc  $ZnO,C_6H_5O_5+3HO$ , dissolves in 58 parts of cold, or 6 of boiling water, and bears a temperature of  $410^\circ$  without decomposition.

Protolactate of iron  $FeO,C_6H_5O_5+3HO$  is prepared by mixing solutions of lactate of ammonia and protochloride of iron, and precipitating by alcohol, or by decomposing lactate of baryta by protosulphate of iron. After having separated the sulphate of baryta, alcohol is added to precipitate the lactate of iron in the form of small yellow aciculæ. The salt is used in medicine.

Lactates of copper and silver are obtained by boiling the carbonates of these metals with a solution of lactic acid, and their formulæ are  $CuO,C_6H_5O_5+2HO$ , and  $AgO,C_6H_5O_5+2HO$ .

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\* It is usually called *lactide*.—J. C. B.

*Lactic ether*  $C_4H_5O, C_6H_5O_2$  is obtained by distilling 2 parts of dried powdered lactate of lime, with a mixture of 2 parts of anhydrous alcohol, and 2 parts of concentrated sulphuric acid, the distillation being arrested at the moment the liquid begins to turn brown. The product is rectified over chloride of calcium, and a colourless liquid obtained, having a peculiar odour, a density of 0.866, and boiling at  $170^\circ$ : lactic ether dissolves in water, alcohol, and ether, and is decomposed by the alkalis, yielding alcohol and lactic acid.

*Butyric Acid*  $C_8H_7O_2, HO$ .

§ 1405. Butyric acid is a colourless liquid, of an extremely disagreeable odour, and the smell of rancid butter is owing to the presence of a small quantity of this acid. It solidifies at the temperature of solid carbonic acid, and boils at  $327.2^\circ$ . It dissolves in all proportions in water, alcohol, and spirit of wood, and its density is 0.963, while that of its vapour is 3.09, its equivalent  $C_8H_7O_2, HO$ , corresponding to 4 vol. of vapour. Butyric acid is inflammable, and chlorine acts on it, yielding two chlorinated butyric acids, of which the formulæ are  $C_8H_5Cl_2O_2, HO$  and  $C_8H_4Cl_3O_2, HO$ .

Butyrates of potassa, soda, and ammonia, are very soluble in water, and crystallize with difficulty.

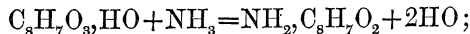
Butyrate of lime is much less soluble hot than cold, and a solution of the salt, saturated at a low temperature, sets into a mass when heated.

The formula of butyrate of baryta, which is deposited from a hot solution, is  $BaO, C_8H_7O_2 + 2HO$ , while that of crystals developed in a cold solution is  $BaO, C_8H_7O_2 + 4HO$ , which latter salt melts in its own water of crystallization.

Butyrate of lead is precipitated in the form of an insoluble liquid, which sets after some time.

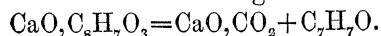
Butyric acid forms a compound ether, which is easily prepared by mixing 100 gm. of butyric acid, 100 gm. of alcohol, and 50 gm. of sulphuric acid, and shaking them for some moments, when a layer of *butyric ether* forms on the surface of the mixture. It is washed with water, and purified by chloride of calcium. Butyric ether, though but slightly soluble in water, is very soluble in alcohol, and boils at  $230^\circ$ , and its formula is  $C_4H_5O, C_8H_7O_2$ .

Ammonia reacts on butyric ether, and produces *butyramid*  $NH_2, C_8H_7O_2$ .



the butyric ether gradually disappearing, and the aqueous solution, when evaporated, yielding pearly crystals of butyramid, which melts at  $239^\circ$ , and sublimes at a higher temperature without decomposition.

Butyrate of lime yields, when heated, an odorous, inflammable liquid, boiling at about  $284^\circ$ , and called *butyrone*. Its formula is  $C_7H_7O$ , and it arises from the following reaction:



By operating on considerable quantities of butyrate of lime, there is formed, with the butyrone, a more volatile liquid, boiling at  $203^{\circ}$ , of the formula  $C_5H_8O_2$ , and which has been called *butyral*. Butyral  $C_5H_8O_2$  is to butyric acid  $C_5H_7O_3$ , HO what aldehyde  $C_4H_4O_2$  is to acetic acid  $C_4H_3O_3$ , HO, which comparison is confirmed by the chemical properties of butyral, since it oxidizes in the air, particularly when aided by platinum sponge, and is converted into butyric acid. It reduces oxide of silver like aldehyde, the metallic silver forming a coating on the surface of the vessel.

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SPIRIT OF WOOD, OR METHYLIC ALCOHOL, AND THE PRODUCTS DERIVED FROM IT.

§ 1406. By subjecting wood to distillation, there is obtained, in addition to the gaseous products, an aqueous acid liquor, which contains a great number of different substances; that which imparts to it its acidity being acetic acid, the method of the extraction of which has been described (§ 1370). There also exists a volatile, inflammable liquid, called *spirit of wood*.

The proportion of this liquid varies according to the nature of the wood and the temperature at which the calcination is effected, and it generally reaches 1 per cent. of the whole quantity of fluid. It is mixed with acetone, aldehyde, methylacetic ether, and two volatile substances to which the names of *mesite* and *xylite* have been given, and lastly, a pitch-like matter is also found. The liquor is saturated with slaked lime, which attacks the acids and a portion of the tarry substances, after which the clarified liquor is decanted and distilled until the first tenth is collected in the receiver. This first product, which contains nearly the whole of the spirit of wood, is again distilled, with a small quantity of lime to decompose the methylacetic ether, and convert it into spirit of wood. The first portions distilled are alone collected, and by continuing these fractioned distillations, highly concentrated spirit of wood is finally obtained, which, when distilled over lime, yields anhydrous spirit of wood. This is sufficient for all purposes of commerce, but in order to separate the pure principle, *methyllic alcohol*, from it, it is treated with twice its weight of melted and powdered chloride of calcium, with which methyllic alcohol forms a crystalline compound, resisting a temperature of  $212^{\circ}$  without decomposition. It is heated in a water-bath, when the greater portion of the foreign products distils over, and the compound of methyllic alcohol with chloride of calcium remains. By treating it with water, it is destroyed, and the methyllic alcohol is set free, and separated by distillation. The product again distilled over quick lime, yields pure and anhydrous methyllic alcohol.

§ 1407. Methyllic alcohol is a colourless liquid, of a peculiar

odour, resembling that of acetic ether, and its density is 0.798, while it boils at  $151.7^{\circ}$ . Its ebullition in a glass vessel is accompanied by violent agitation, which renders its distillation difficult, which is avoided by placing a stratum of mercury at the bottom of the vessel. It burns in the air with a flame resembling that of alcohol, and forms a series of compounds so closely resembling those of ordinary alcohol, that it is impossible to separate the study of these two substances, although their origin is very different, on account of which analogy spirit of wood has been called methylic alcohol (from, *μῆν*, *wine*, and *ῥη*, *wood*.) Its formula is  $C_2H_4O_2$ , and the density of its vapour being 1.041, its equivalent is represented by 4 vol. of vapour like that of alcohol.

Methylic alcohol readily dissolves potassa and soda, and forms, with anhydrous baryta, a crystallizable compound  $BaO, C_2H_4O_2$ , while the formula of its crystalline compound with chloride of calcium is  $2(C_2H_4O_2) 2CaCl$ . Its solvent properties closely resemble those of alcohol, all substances soluble in the latter liquid being equally so in methylic alcohol.

#### ACTION OF SULPHURIC ACID ON METHYLIC ALCOHOL.

§ 1408. On mixing 2 parts of concentrated sulphuric acid with 1 part of methylic alcohol, a great elevation of temperature ensues, and if the acid liquor be saturated with carbonate of baryta, sulphate of baryta separates, and there remains in solution a salt called *sulphomethylate of baryta*,  $BaO, (C_2H_3O, 2SO_3)$  which may be obtained in crystals, by evaporating the liquid to the consistence of syrup, and allowing it to rest in a dry vacuum. All the other sulphomethylates are easily prepared, by double decomposition, from the sulphomethylate of baryta. By carefully decomposing a solution of sulphomethylate of baryta by dilute sulphuric acid, the sulphomethylic acid is obtained isolated, and its solution exposed for a long time in a dry vacuum, yields small acicular crystals of hydrated sulphomethylic acid. All the sulphomethylates are very soluble in water, and when heated are decomposed into the metallic sulphate which remains, and a compound ether, *methylsulphuric ether*  $C_2H_3O, SO_3$ , which shall presently be described.

§ 1409. By mixing 1 part of methylic alcohol with 4 parts of concentrated sulphuric acid, and distilling the mixture, an inflammable gas of the formula  $C_2H_3O$  is disengaged, consisting of *methyltic ether*, which is to methylic alcohol  $C_2H_4O_2$  what ordinary ether  $C_4H_5O$  is to alcohol  $C_4H_6O_2$ . The gas thus obtained is, however, always mixed with small quantities of sulphurous and carbonic acids, which are separated by allowing the gas to remain for some time in contact with caustic potassa.

Methylic ether is a colourless liquid, of a peculiar ethereal smell, and liquid only at a temperature of  $-22^{\circ}$  to  $-40^{\circ}$ ; and its density being 1.61, its formula  $C_2H_3O$  corresponds to 2 vol. of vapour.

Water dissolves about 37 times its volume of it, and it is still more soluble in ordinary and methylic alcohol. As we have been led by chemical reactions to write the formula of alcohol  $C_4H_5O,HO$ , so also we shall be induced to write that of methylic alcohol  $C_2H_3O,HO$ .\*

§ 1410. By distilling 1 part of methylic alcohol with 8 or 10 parts of concentrated sulphuric acid, very little methylic ether is obtained, but an oleaginous liquid distills over, which, when washed several times with water, and then distilled over caustic baryta, presents a composition corresponding to the formula  $C_2H_3O,SO_3$ . It is *methylsulphuric ether*, that is, a compound ether, formed by the combination of methylic ether with sulphuric acid. The corresponding compound  $C_4H_5O,SO_3$  of the alcohol series has recently been obtained.

This product is also obtained by the direct combination of methylic ether  $C_2H_3O$  with anhydrous sulphuric acid, the combination being accompanied with great evolution of heat.

Methylsulphuric ether is a colourless liquid, of the density 1.324, and which boils at  $370.4^\circ$ ; the density of its vapour being 4.37, and its equivalent therefore represented by 2 vol. of vapour. Methylsulphuric ether is slowly decomposed by cold water, but very rapidly by boiling water, the products of decomposition being methylic alcohol  $C_2H_3O,HO$ , and sulphomethylic acid  $C_2H_3O,2SO_3$ .

Dry ammoniacal gas, and the aqueous solutions of ammonia, decompose methylsulphuric ether, forming a white crystallizable substance, which has been called *sulphomethylam*, and also *methylsulphamidic ether*, regarding it as a compound ether, formed by a peculiar acid, *methylsulphamidic*, which has not yet been isolated; the formula of this substance, in fact, may be written



§ 1411. By introducing anhydrous methylic alcohol and anhydrous sulphuric acid, separately, into two open tubes entering a very dry bottle, which is then corked, their vapours combine slowly, and an acid is formed, yielding, with baryta, a soluble salt having the same formula is the sulphomethylate of baryta, but differing in its properties. It is therefore an isomer of sulphomethylic acid.

§ 1412. By causing sulphuric acid, under the most varied circumstances, to act on methylic alcohol, it has hitherto been impossible to obtain a carburetted hydrogen  $C_2H_2$  which shall be to methylic ether  $C_2H_3O$ , what olefiant gas  $C_4H_4$  is to ether  $C_4H_5O$ .

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\* Methylic ether is with more propriety called mether, and regarded as the oxide of a radical,  $C_2H_3$ , or  $H(C_2H_3)$ , which has been isolated, and called methyl. The following series of compounds, called in the text compounds of methylic ether, and methylic acids, should therefore rather be regarded as salts of the oxide of methyl, or mether; the methylic acids being merely acid salts. The names of methylnitric, methyloxalic ether, etc., would then change to respectively nitrate of mether, etc.—*W. L. F.*

*Ethers compounded of Methylic Ether and Methylic Acids.*

§ 1413. Compound methylic ethers are formed under the same circumstances as compound alcoholic ethers, and exhibit the same relations of composition. As in the case of alcohol, two species of combinations of methylic ether with acids are known; neutral compounds, which are *compound methylic ethers* properly so called, and acid compounds, containing a double proportion of acids, and which we shall call *methylic acids*. Certain acids form both kinds of compounds, an example of which has just been shown in sulphuric acid; while others produce only the neutral, and others again only the acid compound.

*Methylnitric Ether,  $C_2H_5O, NO_3$ .*

§ 1414. The preparation of this substance is not so difficult as that of the nitric ether of the vinic series; since nitric acid of commerce may be made to react immediately on methylic alcohol, without any fear of the tumultuous and complicated reactions which this acid exerts on vinic alcohol. The best method of preparing methylnitric ether consists in heating in a retort a mixture of 1 part of methylic alcohol, 1 part of nitrate of potassa, and 2 parts of concentrated sulphuric acid, when an ethereal liquid is obtained which must be rectified several times over litharge and chloride of calcium.

Methylnitric ether is a colourless liquid, of the density 1.182, and which boils at  $154.4^\circ$ ; and the density of its vapour being 2.653, its equivalent  $C_2H_5O, NO_3$  is represented by 4 vol. Methylnitric ether detonates with extreme violence at a temperature slightly above its boiling point, and must therefore be handled with great caution.

A *methylnitrous ether*  $C_2H_5O, NO_2$  would probably be obtained by distilling a mixture of concentrated sulphuric acid and methylic alcohol with nitrate of potassa.

*Methylocarbonic Acid  $C_2H_5O, 2CO_2HO$ .*

§ 1415. By passing a current of carbonic acid gas through a solution of baryta in anhydrous methylic alcohol, a precipitate results in the form of pearl-like spangles, of the formula  $BaO(C_2H_5O, 2CO_2)$ , which is the *carbomethylate of baryta*. The salt is insoluble in methylic alcohol, but dissolves readily in water, being soon decomposed into carbonate of baryta, carbonic acid and methylic alcohol.

Methylocarbonic ether  $C_2H_5O, CO_2$ , has not yet been obtained.

*Methyloxalic Ether  $C_2H_5O, C_2O$ .*

§ 1416. This product is prepared by distilling a mixture of equal parts of crystallized oxalic acid, concentrated sulphuric acid, and methylic alcohol, when a liquid is obtained which, when allowed to evaporate spontaneously, deposits white crystals of methyloxalic acid. The crystals are dried between tissue paper, and distilled over litharge.

Methyloxalic ether is a solid substance, melting at  $123.8^{\circ}$ , and boiling at  $321.8^{\circ}$ . It dissolves in water, alcohol, ether, and methylic ether; and water decomposes it slowly at the ordinary temperature, and rapidly at the boiling point, forming free oxalic acid and methylic alcohol. This ether is decomposed by dry ammoniacal gas, and converted into a crystalline substance, of which beautiful crystals are obtained by redissolving it in alcohol, and which may be considered as a *methyloxamic ether*,  $C_2H_3O_2(NH_2C_2O_2, C_2O_2)$ . If a large quantity of ammonia in solution be used, methylic alcohol and oxamid  $NH_2C_2O_2$  are obtained.

*Methylacetic Ether*  $C_2H_3O, C_4H_3O_3$ .

§ 1417. It is obtained by distilling 2 parts of methylic alcohol with 1 part of monohydrated acetic acid and 1 part of concentrated sulphuric acid. The product is poured over powdered anhydrous chloride of calcium, and shaken frequently, when, by allowing the liquid to rest, two layers are formed, the upper one of which, when distilled over quicklime to retain the sulphurous acid, and then over chloride of calcium to retain a small quantity of methylic alcohol, yields pure methylacetic ether. It is a colourless liquid, having an odour resembling that of acetic ether of the vinic series, and its density is 0.919, while it boils at  $136.4^{\circ}$ . The density of its vapour being 2.57, its equivalent  $C_2H_3O, C_4H_3O_3$  is represented by 4 vol. of vapour. It has been shown (§ 1406) that crude spirit of wood always contains a certain quantity of this substance. Boiling water, and the alkaline solutions particularly, decompose it into methylic alcohol and acetic acid; and it dissolves in 2 parts of water, and mixes in all proportions with vinic and methylic alcohol and with ether.

*Methylochlorocarbonic Ether*  $C_2H_3O, C_2O_3Cl$ .

§ 1418. This ether is formed under circumstances analogous to those in which the corresponding product of the vinic series is produced, that is, by pouring methylic alcohol into a bottle filled with chlorocarbonic gas  $COCl$ . By treating it with water, an oily liquid separates, which is distilled, after being well washed with water, first over chloride of calcium, and then over oxide of lead. It is a colourless liquid, of a suffocating odour. Ammonia dissolved in water decomposes it, chlorohydrate of ammonia and a deliquescent crystalline substance called *urethylan* being formed; which latter, however, may be considered as *methylocarbamic ether*, for its formula can be written  $C_2H_3O, (NH_2, CO, CO_2)$ .

*Methyllobiboracic Ether*  $C_2H_3O, 2BO_3$  and *Trimethylloboracic Ether*  $3C_2H_3O, BO_3$ .

§ 1419. By treating melted and finely powdered boracic acid with methylic alcohol, a combination ensues with elevation of temperature;



and, after driving off the excess of methylic alcohol by heat, there remains as residue a soft, transparent substance, which can be drawn out in threads at the ordinary temperature, consisting of *methylobiboracic ether*  $C_2H_3O, 2BO_3$ . Water decomposes it immediately into hydrated boracic acid and methylic alcohol.

By treating methylic alcohol with chloride of boron, a very volatile and colourless liquid is obtained, having a penetrating smell, and the formula is  $3C_2H_3O, BO_3$ , while its density is 0.955 at  $32^\circ$ , and it boils at  $161.6^\circ$ . The density of its vapour is 3.60.

These two compounds burn with a beautiful green flame.

*Methylosulphocarbonic Ether*  $C_2H_3O, CS_2$ , and *Sulphocarbomethylic Acid*  $C_2H_3O, 2CS_2$ .

§ 1420. By pouring sulphide of carbon into caustic potassa, dissolved in anhydrous amylic alcohol, silky crystals of *sulphocarbomethylate of potassa*  $KO, (C_2H_3O, 2CS_2)$  are formed; and a great number of other *sulphocarbomethylates* are obtained from this salt by double decomposition.

If iodine be added to a solution of sulphocarbomethylate of potassa in methylic alcohol, the temperature rises, while sulphydric acid and oxide of carbon are disengaged.

In addition, iodide of potassium, crystallized sulphur, and a brown oil, which, after two or three rectifications, yields pure *methylosulphocarbonic ether*, are formed. This is an amber-coloured liquid, having a density of 1.143 at  $59^\circ$ , and boiling at about  $338^\circ$ ; and the density of its vapour being 4.266, its equivalent  $C_2H_3O, CS_2$  is represented by 2 volumes of vapour.

*Methylochlorohydric Ether*  $C_2H_3Cl$ .\*

§ 1421. By heating in a flask 2 parts of sea-salt with a mixture of 1 part of methylic alcohol and 3 parts of concentrated sulphuric acid, a colourless gas is disengaged, which is to be left for some time in contact with water, to effect the absorption of the mixed sulphurous acid and methylic ether. This gas, which does not liquefy at a cold of  $-0.4^\circ$ , is *methylochlorohydric ether*. Its density is 1.728, and its equivalent  $C_2H_3Cl$  corresponds to 4 volumes of vapour. It burns with a flame edged with green; and water dissolves about 3 times its volume of it.

*Methyliodohydric Ether*  $C_2H_3I$ .

§ 1422. It is formed by pouring 8 parts of iodine into 12 or 15 parts of methylic alcohol, and gradually adding 1 part of phosphorus, and then applying heat to distil the liquor. The liquid collected in the receiver is shaken with water, the ether is precipitated, washed

\* According to the more probable theory, this substance would be chloride of methyl.—W. L. F

several times with water, and then distilled, first over chloride of calcium, and then over oxide of lead. It is a colourless liquid, boiling between  $104^{\circ}$  and  $122^{\circ}$ ; while its density is 2.237 at  $69.8^{\circ}$ .

*Methylofluohydric Ether*  $C_2H_3Fl$ .

§ 1423. This simple ether, the corresponding one of which in the vinic series is not yet known, is prepared by heating in a retort, methylosulphuric ether  $C_2H_3O,SO_3$  with fluoride of potassium, or also with fluoride of calcium reduced to an impalpable powder; when a colourless gas is disengaged, of an agreeable ethereal smell, burning with a bluish flame, and of which the density is 1.186; while its equivalent  $C_2H_3Fl$  corresponds to 4 volumes. Water dissolves  $1\frac{1}{2}$  time its volume of it.

*Methylocyanohydric Ether*  $C_2H_3Cy$ .

§ 1424. In order to obtain this ether, it is sufficient to distil methylosulphuric ether with cyanide of potassium, or finely pulverized cyanide of mercury; when it is obtained as a liquid, insoluble in water, and very poisonous.

*Methylosulphydric Ether*  $C_2H_3S$  and its Compounds.

§ 1425. Methylosulphydric ether is prepared by passing a current of methylochlorohydric ether  $C_2H_3Cl$  through an alcoholic solution of monosulphide of potassium, heating the liquid, and collecting the distilled products in a well-cooled receiver; after which they are washed with water and distilled over chloride of calcium.

Methylosulphydric ether is a very volatile liquid, of an extremely disagreeable smell, and its density is 0.846 at  $69.8^{\circ}$ , while it boils at  $105.8^{\circ}$ . The density of its vapour is 2.115, and its equivalent  $C_2H_3S$  corresponds to 2 volumes of vapour, like methylic ether  $C_2H_3O$ .

Methylosulphydric ether is a simple ether, which forms a great number of compound ethers by combining with electro-negative sulphides; and the principal of these compound ethers are:

§ 1426. *Methylosulphydric Alcohol*  $C_2H_3S,HS$ , or methylic alcohol  $C_2H_3O,HO$ , in which the 2 equivalents of oxygen are replaced by 2 equivalents of sulphur; which is obtained by passing a current of methylochlorohydric ether through an alcoholic solution of sulphhydrate of sulphide of potassium, and then distilling the mixture. It is also prepared by distilling a mixture of sulphomethylate of potassa  $KO,(C_2H_3O,2SO_3)$  with a solution of sulphhydrate of sulphide of potassium; the distilled product being washed with water, and rectified over chloride of calcium. Methylosulphydric alcohol, also called *methylic mercaptan*, is a colourless liquid, of an extremely fetid odour, and very volatile, for it boils at  $69.8^{\circ}$ . It is decomposed by contact with red oxide of mercury, and yields a crystallized product, in which the sulphydric acid is replaced by 1 equivalent.

valent of sulphide of mercury  $\text{Hg}_2\text{S}$ ; analogous products being obtained with several other metallic sulphides.

§ 1427. *Sulphocarbomethylosulphydric Ether*  $\text{C}_2\text{H}_3\text{S}, \text{CS}_2$  is obtained by distilling a concentrated solution of sulphomethylate of lime  $\text{CaO}, (\text{C}_2\text{H}_3\text{O}, 2\text{SO}_3)$  with a solution, also concentrated, of sulphocarbonate of sulphide of potassium  $\text{KS}, \text{CS}_2$ , and rectifying the liquid over chloride of calcium. It is a yellowish liquid, of a density of 1.159 at  $64.4^\circ$ , while it boils at  $399.2^\circ$ . The density of its vapour being 4.650, its equivalent  $\text{C}_2\text{H}_3\text{S}, \text{CS}_2$  is represented by 2 volumes of vapour: it is methylocarbonic ether  $\text{C}_2\text{H}_3\text{O}, \text{CO}_2$ , hitherto unknown, the oxygen of which is replaced by equivalent quantities of sulphur.

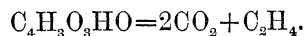
§ 1428. By replacing, in the preparation of methylosulphydric ether, the alcoholic solution of monosulphide of potassium, by an alcoholic solution of bisulphide of potassium, a slightly yellowish liquid is obtained, of an extremely disagreeable and persistent alliaceous odour; while its density is 1.046 at  $64.4^\circ$ , and it boils at  $240.8^\circ$ . The formula of this substance being  $\text{C}_2\text{H}_3\text{S}_2$ , it may be considered as methylosulphydric ether  $\text{C}_2\text{H}_3\text{S}$ , combined with 1 equivalent of sulphur: the density of its vapour is 3.310, and its equivalent corresponds to 2 volumes of vapour.

Lastly, by substituting pentasulphide for the bisulphide of potassium, there results a product still more sulphuretted, of which the formula is  $\text{C}_2\text{H}_3\text{S}_3$ .

*Protocarburetted Hydrogen  $\text{C}_2\text{H}_4$ , or Marsh Gas.*

§ 1429. Protocarburetted hydrogen evidently belongs to the methylic series, and may be considered as the starting point of this series. By causing chlorine to act on this gas, products are obtained which are identical with those afforded by methylochlorohydric ether  $\text{C}_2\text{H}_3\text{Cl}$ , and it is not to be doubted, although this is not yet proved, that by causing suitable volumes of protocarburetted hydrogen and chlorine to react on each other, methylochlorohydric ether itself will be obtained. Now, methylochlorohydric ether, treated with an alcoholic solution of potassa, yields methylic alcohol; and it has been mentioned (§ 1390) that the vinic series may also be regarded as derived from a carburetted hydrogen  $\text{C}_4\text{H}_6$ , which is as yet unknown.

When vapours of monohydrated acetic acid  $\text{C}_4\text{H}_3\text{O}_3, \text{HO}$  are poured through a glass tube containing platinum-sponge, and heated to  $750^\circ$ , the acetic acid is decomposed into carbonic acid and protocarburetted hydrogen,



A similar decomposition takes place by heating acetic acid in contact with an excess of alkali; but in that case the carbonic acid remains combined with the alkali, and the protocarburetted hydrogen

alone is disengaged. The most economical manner of preparing the gas consists in heating 4 parts of crystallized acetate of soda with 10 parts of an alkaline mixture composed of 2 parts of caustic potassa and 3 parts of quicklime. In order to make the mixture, the 2 parts of potassa are dissolved in a small quantity of water and sprinkled over with the 3 parts of pulverized quicklime; and the paste is then heated to a dull-red to drive off the excess of water.

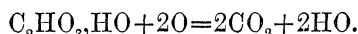
Protocarburetted hydrogen also arises spontaneously from marsh mud (§ 265) and from layers of bituminous coal.

It has never been liquefied at any temperature, and its density is 0.559, while its equivalent  $C_2H_4$  corresponds to 4 vol. of gas, and it burns with a bluish flame, which is much less brilliant than that of bicarburetted hydrogen.

#### PRODUCTS OF THE OXIDATION OF METHYLIC ALCOHOL.

##### *Formic Acid* $C_2HO_3HO$ .

§ 1430. Methyl alcohol oxidizes, at the expense of the oxygen of the air, in the presence of platinum-sponge, and, like alcohol, it exchanges, in this case, 2 equiv. of hydrogen for 2 equiv. of oxygen,\* producing a peculiar acid  $C_2HO_3HO$ , called *formic*, a large portion of which is, however, destroyed by contact with the platinum-sponge, and, especially if the temperature be elevated, complete combustion and the formation of carbonic acid ensue:



But formic acid is obtained in a great number of chemical reactions, in which certain organic substances are subjected to oxidizing agents; by heating, for example, a mixture of peroxide of manganese and dilute sulphuric acid, with alcohol, sugar, fecula, tartaric acid, etc., a portion of the organic substance being completely converted into water and carbonic acid, while the other is imperfectly oxidized and produces formic acid. When any considerable quantity of formic acid is to be prepared, 2 kilog. of sugar are dissolved in 10 litres of water, and 6 kilog. of sulphuric acid being gradually added, the mixture is poured into the cucurbit of an alembic, at the bottom of which have been placed 6 kilog. of peroxide of manganese. A lively effervescence ensues immediately, owing to the evolution of carbonic acid, and when it lessens, the capital is adjusted and distillation effected, but it is arrested when 5 or 6 litres of liquid are obtained. This liquid, in which the formic acid is concentrated, is

\* It is more rational to assume, in the case of both acetic and formic acids, that the alcohol takes up 4 equiv. of oxygen and gives off 3 equiv. of water, because the substitution of oxygen for hydrogen in combinations is scarcely admissible.

Vinic alcohol  $C_4H_6O_4$ , by taking up  $O_4$ , becomes  $C_4H_6O_8$ , and, by losing 3HO, assumes the formula of acetic acid  $C_4H_3O_5 + aq$ .

In like manner, methyl alcohol  $C_2H_4O_2$  becomes  $C_2H_4O_6$  by gaining  $O_4$ , and is converted into formic acid  $C_2HO_3 + aq$ . by giving off 3HO.—*W. L. F.*

saturated with milk of lime and the formiate of lime crystallized by evaporation. The salt thus forms only crystalline crusts; and by distilling it with more or less concentrated sulphuric acid, formic acid also more or less concentrated is obtained.

If formic acid is to be obtained at its maximum of concentration, the formiate of lime must be converted into formiate of lead, by adding acetate of lead to the solution of formiate of lime; when the formiate of lead, being but slightly soluble in cold water, is almost wholly deposited, and may be purified by dissolving it in boiling water, which deposits it, on cooling, in small prismatic crystals.

Formiate of lead, well dried, is introduced into a long glass tube, heated by some coals, and through which a current of sulphydric acid is passed, when sulphide of lead is formed, while monohydrated formic acid condenses in the receiver. It is a colourless liquid, of a penetrating and characteristic odour, and it solidifies at a few degrees below  $32^{\circ}$ , while it boils at  $212^{\circ}$ . Its density is 1.235, and the density of its vapour being 1.556, its equivalent  $C_2H_3O_3.HO$  is represented by 4 volumes of vapour.

Monohydrated formic acid is highly caustic, and produces blisters on the skin. In combining with water, the first portions of water added elevate its boiling point; with the addition of 20.7 of water, that is 1 equiv., it boils at  $222.8^{\circ}$ . An excess of concentrated sulphuric acid decomposes formic acid into oxide of carbon and water. At the boiling point, formic acid reduces several metallic oxides, particularly the oxides of silver and mercury.

Formiate of potassa and soda are very soluble and deliquescent.

Formiate of baryta dissolves in 4 parts of water, and crystallizes readily; the formula of its crystals being  $BaO.C_2H_3O_3$ .

Formiate of lime dissolves in 10 parts of water, and is nearly as soluble in hot as in cold water.

Formiate of lead requires 36 to 40 parts of cold water for solution, but dissolves more freely in hot water, and its crystals are anhydrous.

By double decomposition, a formiate of silver may be obtained which is destroyed by being boiled with water.

§ 1431. Formic ether  $C_4H_5O.C_2H_3O_3$  of the vinic series is obtained by heating a mixture of 7 parts of dry formiate of soda, 10 parts of concentrated sulphuric acid, and 9 parts of alcohol. It is made on a larger scale and cheaply, by mixing, in a large retort, 80 parts of starch, 120 of ordinary alcohol at 0.85, 120 parts of water, 304 of peroxide of manganese, and 240 of concentrated sulphuric acid. Heat is applied gently, and, when the reaction is fully established, the fire is removed, and the sides of the retort cooled with moist cloths, when a stratum of formic ether separates, which is removed and treated with milk of lime to free it from acids, and subsequently distilled over chloride of calcium.

Formic ether is a colourless liquid, of a mild taste, of a density of

0.912, and boiling at  $128.1^{\circ}$ , which dissolves in 10 parts of water, and mixes in all proportions with alcohol. It should be remarked that formic ether  $C_4H_5O, C_2HO_3$  is isomeric with methylacetic ether  $C_2H_3O, C_4H_5O_3$ . Formic ether, treated with chlorine in diffused light, forms a chlorinated ether, of the formula  $C_4H_3Cl_2O, C_2HO_3$ , and, by exhausting the action of the chlorine in the sun, a *perchlorinated chloroformic ether*  $C_4Cl_5O, C_2ClO_3$  is obtained.

*Methyloformic ether*  $C_2H_3O, C_2HO_3$  is prepared in the same manner as that of the vinic series, except that spirit of wood is substituted for alcohol, and it is an ethereal, very mobile liquid, which boils at about  $98.6^{\circ}$ .

*Methylal*  $C_6H_8O_4$ .

§ 1432. It has not yet been found possible to obtain aldehyde of the methylic series, the formula of which would be  $C_2H_2O_2$ . By distilling a mixture of methylic acid and alcohol over peroxide of manganese, there results a mixture of several volatile liquids, in which methyloformic ether and a peculiar liquid, called *methylal*, predominate. The latter being dissolved in water, and potassa added, the alkali decomposes the methyloformic ether, while the methylal separates in the form of a liquid layer floating on the surface, which is purified by distillation over chloride of calcium. Methylal boils at  $107.6^{\circ}$ , and corresponds to acetal. Its formula being  $C_6H_8O_4$ , it may be regarded as resulting from the union of 3 molecules of methylic ether, of which one has taken 1 equiv. of oxygen in the place of 1 equiv. of hydrogen.\*

ACTION OF CHLORINE ON COMPOUNDS OF THE METHYLIC SERIES.

*Products of the Action of Chlorine on Methylochlorohydric Ether and on Protocarburetted Hydrogen.*

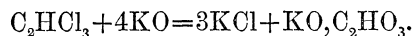
§ 1433. Chlorine acts with more difficulty on chlorohydric ether of the methylic series than on that of the vinic series, the reaction ensuing only when assisted by the direct rays of the sun; and as these products are more volatile, greater care is required in cooling the receivers. The apparatus described (§ 1387) and represented by fig. 680 is used.

By maintaining the methylochlorohydric ether in excess, the bottle C, (fig. 680), which should be kept in a refrigerating mixture, receives a very volatile liquid, which should be purified by distillation over concentrated sulphuric acid, and then over quicklime, and which is *monochlorinated methylochlorohydric ether*  $C_2H_3Cl_2$ . The odour of this product resembles that of Dutch liquid, and its density

\* Here again it is unnecessary to assume the highly improbable substitution of oxygen for hydrogen, since the reaction is very simply explained by allowing 3 equiv. of methylic ether  $C_2H_5O_2$  to gain 2 equiv. of oxygen, forming  $C_6H_8O_4$ , and then to lose 1 equiv. of water, which gives methylal  $C_6H_8O_4$ .—W. L. F.

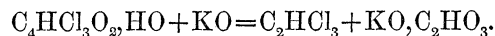
is 1.344 at 64.4°, while it boils at 86.9°. The density of its vapour being 2.94, its equivalent  $C_2H_2Cl_2$  is represented by 4 volumes of vapour, like that of methylochlorohydric ether  $C_2H_3Cl$ .

§ 1434. The second product of the action of chlorine on methylochlorohydric ether is a liquid having a density of 1.491 at 62.6°, and boiling at 141.8°; the composition of which is represented by the formula  $C_2HCl_3$ , corresponding to 4 vols. of vapour. This is *bichlorinated methylochlorohydric ether*, more commonly known as *chloroform*, which name has been given to it because, in contact with an alcoholic solution of potassa, it yields chloride of potassium and formiate of potassa,

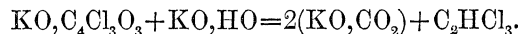


Chloroform is produced in several other chemical reactions, and particularly when a solution of hypochlorite of lime is made to react on alcohol or acetone. This product has been extensively manufactured since the discovery of its power in effecting the insensibility of patients during surgical operations.

Chloroform is also obtained by decomposing hydrated chloral  $C_4HCl_3O_2, HO$  by a solution of potassa,



Lastly, chloroform is produced when the chloracetates are heated in the presence of an excess of hydrated alkali,



It is readily and economically prepared, by pouring 35 to 40 litres of water into the cucurbit of an alembic, heating the water to 106°, and adding first 5 kilog. of quicklime, and subsequently 10 kilog. of hypochlorite of lime of commerce; and lastly, by pouring in  $1\frac{1}{2}$  litre of alcohol at 0.85, and, after having mixed it well, and adjusted the capital, heating the liquid to boiling. As soon as distillation commences, the fire is slackened and the process allowed to continue spontaneously, when an aqueous liquid condenses in the receiver, at the bottom of which a heavier liquid, chloroform, is formed. It is separated and purified by distillation over chloride of calcium; and the process just described yields about 600 gm. of chloroform.

§ 1435. Chloroform, subjected to the action of chlorine, in the light of the sun, until chlorohydric acid is no longer disengaged, loses its last equivalent of hydrogen, while *perchlorinated methylochlorohydric ether*  $C_2Cl_4$ , which is a new chloride of carbon, is formed. This compound is liquid at the ordinary temperature, but at 9.4° solidifies into a pearly crystalline mass; and it boils at 172.4°. Its density is 1.599; the density of its vapour being 5.80, its equivalent is likewise represented by 4 volumes of vapour.

§ 1436. By exposing to the rays of the sun a bottle containing a

mixture of protocarburetted hydrogen, and chlorine in excess, a liquid condenses on the sides, which is a mixture of the various chlorinated methylochlorohydric ethers just described, comprising principally chloroform  $C_2HCl_3$  and chloride of carbon  $C_2Cl_4$ . The first chlorinated product, methylochlorohydric ether  $C_2H_3Cl$ , would probably be obtained by introducing the two gases in an apparatus resembling that of fig. 680, maintaining the protocarburetted hydrogen in excess, and then passing the gases through a tube cooled by solidified carbonic acid, in order to condense the gaseous ether. In all cases, it is proved that, by the action of chlorine and protocarburetted hydrogen  $C_2H_4$ , the same products are obtained as by the action of chlorine on methylochlorohydric ether  $C_2H_3Cl$ , and it is correct to regard this substance as the starting point of the series. Thus, we have

Protocarburetted hydrogen .....	$C_2H_4$ , a non-liquefiable gas.
Methylochlorohydric ether .....	$C_2H_3Cl$ , liquefying at a very low temperature.
Monochlorinated methylochlorohydric ether .....	$C_2H_2Cl_2$ , boiling at $86.9^\circ$ .
Bichlorinated methylochlorohydric ether, or chloroform .....	$C_2HCl_3$ , boiling at $141.8^\circ$ .
Perchlorinated methylochlorohydric ether .....	$C_2Cl_4$ , boiling at $172.4^\circ$ .

§ 1437. But again, it is possible, by operating on chloride of carbon  $C_2Cl_4$ , and by proper chemical reactions, to substitute hydrogen for the chlorine, and ascend from chloride of carbon to protocarburetted hydrogen, passing through all the intermediate products: in order to prove which, it is sufficient to introduce into a flat-bottomed flask a solution of chloride of carbon in aqueous alcohol, and then to add an amalgam of potassium. On communicating the flask successively with two U-tubes, the first of which is kept at a temperature of about  $86^\circ$ , and the second cooled by a mixture of ice and salt, then with a bulb-apparatus filled with water, and lastly with a conducting-tube which leads the gases into a bell-glass over the water-cistern, and heating the flask, the chloride of carbon is decomposed, chloride of potassium and caustic potassa being formed; and the chlorine abstracted is replaced by hydrogen arising from the decomposition of the water.

Bichlorinated methylochlorohydric ether  $C_2HCl_3$  condenses chiefly in the first U-tube, and in the second the monochlorinated methylochlorohydric ether  $C_2H_2Cl_2$ , while the water in the bulb-apparatus dissolves the methylochlorohydric ether  $C_2H_3Cl$ , which may be separated by saturating it with chloride of calcium; and lastly, protocarburetted hydrogen is collected in the bell-glass.

This inverse transformation has not hitherto succeeded on the corresponding series of chlorohydric ether of alcohol; but would be



particularly interesting, as it would enable the preparation of the carburetted hydrogen  $C_4H_6$  which is still wanting in the series.

*Bromoform, Iodoform, and Sulphoform.*

§ 1438. By treating alcohol with bromine, a product corresponding to chloral is obtained, which is decomposed by alkaline solutions, and yields *bromoform*  $C_2HBr_3$ .

*Iodoform*  $C_2HI_3$  is obtained by pouring a solution of caustic potassa, or carbonate of potassa, into alcohol saturated with iodine, until the liquid is discoloured; when, by adding a large quantity of water, the iodoform is precipitated in the form of small crystalline spangles, which are purified by redissolving them in alcohol and evaporating the liquid.

By distilling 1 part of iodoform with 3 parts of sulphide of mercury, a yellow oleaginous liquid is obtained, constituting *sulphoform*  $C_2HS_3$ .

*Action of Chlorine on Methylc Ether  $C_2H_5O$ .*

§ 1439. The action of chlorine on methylc ether is excessively violent, even in diffused light; and the experiment, being dangerous, must be carefully conducted, in order to prevent the apparatus from bursting to pieces. Figure 682 represents the apparatus most suit-

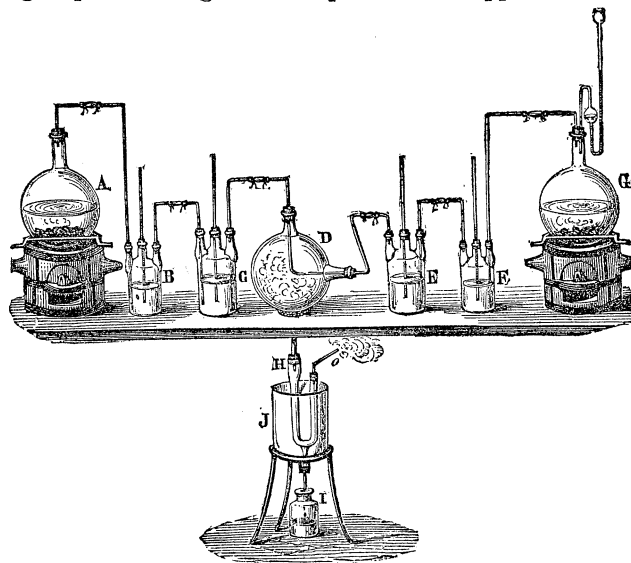


Fig. 682.

able to the production of any considerable quantity of the product. Methylc ether is prepared by heating in a flask A (fig. 682) a mixture of 1 part of wood-spirit and 4 parts of concentrated sulphuric

acid; allowing the gas to traverse a first washing-bottle B containing water, then a second bottle C containing a solution of potassa in order to retain the sulphurous and carbonic acids, and lastly, a long tube filled with chloride of calcium to dry the gas. (This tube is not represented in the figure.) The chlorine is prepared in the flask G by the reaction of chlorohydric acid on peroxide of manganese, and is washed in the water of the bottle F, and dried by passing through concentrated sulphuric acid contained in the bottle E. The two gases, which are brought together in the flask D, escape through a refrigerator H, made very cold by ice, into the atmosphere by the opening *o*. The liquids which condense in the flask D and in the refrigerator H fall into the bottle I, which should be entirely independent of the apparatus, so that if the latter should burst, the products already obtained will not be lost.

The apparatus should be arranged in a well-lighted place, but protected from the direct rays of the sun; and, though the reaction is sometimes long in being established, when once commenced, it continues with great energy. The operator should then regulate the evolution of the two gases with great care: they should meet in such proportion as to destroy each other, immediately, on reaching the flask D; for if one of the gases should flow too freely, as, for example, if the flask were to become coloured by chlorine, which would require a more rapid disengagement of methylic ether, an explosion would inevitably ensue. In order to prevent this accident, the current of chlorine must be lessened by opening one of the washing-bottles E or F, and the ether must be allowed to flow very slowly until the flask D is deprived of colour; after which the gases would be made to flow.

The bottle I is found to contain a very volatile liquid, of a suffocating odour and exciting to tears, which exhales acid fumes by being decomposed by the moisture of the air. Its density at  $68^{\circ}$  is 1.315, while it boils at  $221^{\circ}$ , and cold water decomposes it, though slowly. This liquid is monochlorinated methylic ether  $C_2H_5ClO$ , the formula of which corresponds to 2 volumes of vapour, like that of methylic ether  $C_2H_5O$ , from which it is derived.

This product, subjected to the action of chlorine, exchanges 1 equivalent of hydrogen for 1 equivalent of chlorine, and becomes *bichlorinated methylic ether*, the density of which is 1.606 at  $68^{\circ}$ , while it boils at about  $266^{\circ}$ ; its equivalent  $C_2HCl_2O$  corresponding likewise to 2 volumes of vapour.

Finally, by again exposing this new product to the action of chlorine, in the rays of the sun, its last equivalent of hydrogen is replaced by 1 equivalent of chlorine, forming *perchlorinated methylic ether*  $C_2Cl_3O$ , which product has not maintained a state of concentration similar to that of the two preceding, and that of methylic ether  $C_2H_5O$ , for its equivalent corresponds to 4 volumes of vapour. There has been either a doubling of the original mole-

cule, or a separation of the molecules, so that the same number of molecular groups now occupy a double space; which change of molecular arrangement is manifested by an anomaly in the boiling point. It has always hitherto been observed that when a molecular group is modified merely by the substitution of 1 equivalent of chlorine for 1 equivalent of hydrogen, its boiling point rises; which circumstance is not true for terchlorinated methylic ether, compared with bichlorinated methylic ether; the boiling point of the latter being  $266^{\circ}$ , while that of the former is about  $212^{\circ}$ .

*Action of Chlorine on Methylosulphydic Ether.*

§ 1440. Chlorine readily acts on methylosulphydic ether, which gradually exchanges its oxygen for equivalent quantities of chlorine, and the final product is *perchlorinated methylosulphydic ether*  $C_2Cl_3S$ .

*Action of Chlorine on the Compound Methylic Ethers.*

§ 1441. A large number of compound ethers of the methylic series can exchange more or less completely their hydrogen for equivalent quantities of chlorine.

Thus methyloxalic ether  $C_2H_3O, C_2O_3$  furnishes

A bichlorinated methyloxalic ether.....  $C_2HCl_2O, C_2O_3$ ,

And a perchlorinated “ “ .....  $C_2Cl_3O, C_2O_3$ .

Methylacetic ether  $C_2H_3O, C_4H_3O_3$  also yields

A bichlorinated methylacetic ether.....  $C_2HCl_2O, C_4H_3O_3$ ,

And a perchlorinated “ “ ....  $C_2Cl_3O, C_4Cl_3O_3$ .

It has been shown that formic ether of the vinic series  $C_4H_5O, C_2HO_3$  presents the same elementary composition as methylacetic ether  $C_2H_3O, C_4H_3O_3$ , although the two substances differ materially in their physical and chemical properties; and the composition of the perchlorinated products of the two ethers should therefore be similar: not only are they so, but they are identical, constituting one and the same substance, and no longer exhibiting the diversity of their origin. We have already mentioned an analogous case. Dutch liquid  $C_2H_3Cl, HCl$  is isomeric with monochlorinated chlorohydric ether  $C_4H_4Cl_2$ , while the two substances differ distinctly in their physical and chemical properties; but when treated with chlorine, they both yield the same final product, chloride of carbon  $C_4Cl_6$ .

Methyloformic ether yields with chlorine two chlorinated ethers:

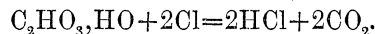
Bichlorinated methyloformic ether.....  $C_2HCl_2O, C_2HO_3$ ,

And perchlorinated “ “ .....  $C_2Cl_3O, C_2ClO_3$ .

This last ether is liquid, boils at about  $356^{\circ}$ , and is isomeric with chlorocarbonic gas  $COCl$ ; into which it is entirely converted, by passing its vapour into a tube heated to a temperature above  $572^{\circ}$ .

*Action of Chlorine on Formic Acid.*

§ 1442. No chlorinated formic acid is known, and when monohydrated formic acid  $C_2HO_3HO$  is treated with chlorine, the equivalent of water is always decomposed, chlorohydric and carbonic acids being formed:



But it has been shown (§§ 1431 and 1441,) that the formic acid which exists in formic and methyloformic ethers can exchange its hydrogen for chlorine.

§ 1443. It will be seen from the preceding observations that the compounds of the methylic series may be considered as being produced by the same molecule  $C_2H_4$ , that of protocarburetted hydrogen, or marsh gas, in which one or several equivalents of hydrogen are replaced by a corresponding number of other elements, such as oxygen, sulphur, chlorine, etc. etc. In order to render this method of generation evident, we have collected into a single table all the known products of the methylic series.

TABLE OF COMPOUNDS DERIVED FROM CARBURETTED HYDROGEN  $C_2H_4$ , OR FROM METHYLIC ETHER  $C_2H_3O$ .

Protocarburetted hydrogen, or..... $C_2H_4$       2 vols.  
Marsh Gas, the starting point of the series.

## SIMPLE ETHERS.

Methylic ether.....	$C_2H_3O$	2	“
Methylsulphydic ether.....	$C_2H_3S$	2	“
Methylochlorohydric ether.....	$C_2H_3Cl$	4	“
Methylbromohydric ether.....	$C_2H_3Br$	4	“
Methylodohydric ether.....	$C_2H_3Io$	4	“
Methylhydrocyanic ether.....	$C_2H_3Cy$	4	“
Methylsulphohydrocyanic ether.....	$C_2H_3SCy$	4	“

## COMPOUND ETHERS.

*Alcohols.*

Methylic alcohol, or wood-spirit.....	$C_2H_3O, HO$	4	“
Methylsulphydic alcohol.....	$C_2H_3S, HS$	4	“
Methyloplumbic      “ .....	$C_2H_3S, PbS$		
Methylomercuric      “ .....	$C_2H_3S, Hg_2S$		

*Compound Ethers, properly so called.*

General formula ( $\bar{A}$ representing the acid).....	$C_2H_3O, \bar{A}$	2 or 4	vols.
Methylbaboracic ether.....	$C_2H_3O, 2BO_3$		
Trimethylboracic      “ .....	$3C_2H_3O, BO_3$	4	“

*Methylic Acids.*

General formula of methylic acids formed by the monobasic acids $\bar{A}$ .....	$(C_2H_3O + HO), 2\bar{A}$
Formula of the methylic acids produced by the tribasic acids, such as $PO_3, 3HO$ .....	$(C_2H_3O + 2HO), PO_4$

PRODUCTS DERIVED SUCCESSIVELY FROM METHYLIC ETHER  $C_2H_3O$ .*1st. By Oxidation.*

Methylic ether.....	$C_2H_3O$	2 vols.
Methylal.....	$(2C_2H_3O, C_2H_2O_2)$	4 “
.....		
Anhydrous formic acid.....	$C_2HO_3$	unknown.
Remains combined with the water formed and yields		
Hydrated formic acid.....	$C_2HO_3, HO$	4 “
But corresponding to methylic alcohol.....	$C_2H_3O, HO$	4 “

*2d. By the Action of Chlorine.*

Methylic ether.....	$C_2H_3 O$	2 “
Monochlorinated methylic ether.....	$C_2H_3ClO$	2 “
Bichlorinated “ “ .....	$C_2HCl_2O$	2 “
Perchlorinated “ “ .....	$C_2Cl_3 O$	4 “

PRODUCTS DERIVED FROM METHYLOSULFHYDRIC ETHER  $C_2H_3S$ .*By the Action of Chlorine.*

Methylsulfhydic ether.....	$C_2H_3S$	2 vols.
.....		
Perchlorinated methylsulfhydic ether.....	$C_2Cl_3S$ .	

PRODUCTS DERIVED FROM PROTOCARBURETTED HYDROGEN  $C_2H_4$ , OR  
FROM METHYLOCHLOROHYDRIC ETHER  $C_2H_3Cl$ .*By the Action of Chlorine.*

Protocarburetted hydrogen.....	$C_2H_4$	4 vols.
Methylochlorohydric ether.....	$C_2H_3Cl$	4 “
Monochlorinated methylochlorohydric ether.....	$C_2H_2Cl_2$	4 “
Bichlorinated do., or chloroform.....	$C_2HCl_3$	4 “
Perchlorinated do., “ .....	$C_2Cl_4$	4 “

PRODUCTS DERIVED FROM METHYLIC ALCOHOL  $C_2H_3O, HO$ .*1st. By the Action of Oxygen.*

Methylic alcohol.....	$C_2H_3O, HO$	4 vols.
.....		
Formic acid .....	$C_2HO_3, HO$	4 “

*2d. By the Action of Chlorine.*

Products unknown.....

PRODUCTS DERIVED FROM AQUEOUS METHYLIC ALCOHOL  
 $C_2H_3O, HO + HO$ .*By the Action of Chlorine.*

Formic acid.....  $C_2HO_3, HO$ .

An excess of chlorine converts the formic acid, by its oxidizing action, into carbonic acid.

Aqueous methylic ether  $C_2H_3O + 2HO$  yields the same products.

## PRODUCTS DERIVED FROM COMPOUND METHYLIC ETHERS.

*By the Action of Chlorine.*

On Methyloxalic ether.....	$C_2H_3$	$O, C_2$	$O_3$ .
Bichlorinated methyloxalic ether.....	$C_2H$	$Cl_3O, C_2$	$O_3$ .
Perchlorinated “ “ .....	$C_2$	$Cl_3O, C_2$	$O_3$ .
On Methylacetic ether.....	$C_2H_3$	$O, C_4H_3O_3$ .	
Bichlorinated methylacetic ether .....	$C_2H$	$Cl_3O, C_4H_3O_3$ .	
Perchlorinated “ “ .....	$C_2$	$Cl_3O, C_4H_3O_3$ .	
On Methyloformic ether.....	$C_2H_3$	$O, C_2H$	$O_3$ .
Bichlorinated methyloformic ether.....	$C_2H$	$Cl_3O, C_2H$	$O_3$ .
Perchlorinated “ “ .....	$C_2$	$Cl_3O, C_2ClO_3$ .	

§ 1444. Chemists have formed, for the methylic series, hypotheses analogous to those proposed for the vinic series. Some regard all simple methylic ethers as produced by the combination of the same radical  $C_2H_3$ , or *methylen*, with 1 equivalent of oxygen, sulphur, chlorine, etc. etc., in which case methylic ether becomes a monohydrate of methylen  $C_2H_3.HO$ , and methylic alcohol its bi-hydrate  $C_2H_3.2HO$ . This radical is entirely hypothetical, since as yet no carburetted hydrogen of the formula  $C_2H_3$  is known which yields by direct combination, either with water or with chlorohydric acid, a simple ether of the methylic series; a condition indispensable, nevertheless, to enable it to be considered as the radical of the series. Moreover, the methylic and vinic series are so similar that their formula cannot be written in two different ways, and we have incontestably proved (§ 1401) that bicarburetted hydrogen  $C_4H_4$  could not be considered as pre-existing in the state of a radical in vinic ethers.

Other chemists consider methylic ether  $C_2H_3O$  as the oxide of a radical  $C_2H_3$ , which they call *methyl*, and of which methylochlorohydric ether is then the chloride; but as methyl is not any better known than is ethyl and methylen, we see no advantage in resorting to hypotheses of these unknown radicals, especially for the methylic series, which may be as easily derived, by means of substitution, from a perfectly well known hydrocarbon, protocarburetted hydrogen  $C_2H_4$ . We have shown it, in fact, (§ 1436,) to be very probable that, by causing chlorine, in proper proportions, to act upon carburetted hydrogen  $C_2H_4$ , methylochlorohydric ether  $C_2H_3Cl$  would be obtained: now, the latter is decomposed by contact with alkaline solutions, and yields wood-spirit, whence the whole methylic series may be subsequently derived.\*

\* Referring the reader, on the subject of the radicals of ether and mether, back to the note to § 1401, (page 568,) it now only remains to describe the radical methyl, the isolation of which renders the correctness of the French theory extremely doubtful.

*Methyl*  $C_2H_3$ .

Methyl is given off at the positive pole, in decomposing a concentrated solution of acetate of potassa by a powerful galvanic current, while at the negative pole

OF CERTAIN ACIDS WHICH EXIST IN THE JUICES OF  
VEGETABLES.

§ 1445. We shall describe in this chapter certain acids which are found ready formed in the juices of vegetables, and which have not been included in any group of substances of analogous composition, as chemists have succeeded in doing for acetic, formic acid, etc. etc.

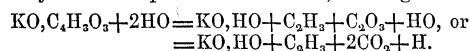
OXALIC ACID  $C_2O_3, HO$ .

§ 1446. Of these acids, one of the most important is oxalic, of which the properties were described (§ 259) when treating of the compounds of carbon with oxygen, among which oxalic acid is ranked on account of the composition it presents in anhydrous salts. Oxalic acid is found in a large number of vegetables, which frequently, as in the case of sorrel,\* owe their acid taste to its presence. In the Black Forest (Southern Germany) it is obtained from certain species of rumex, by pounding the plant in troughs and expressing its juice; after which the residue is moistened with water and expressed a second time. The liquid is clarified with clay, decanted and evaporated to crystallization; when crystals of binoxalate and quadroxalate of potassa, (§ 451,) called in commerce *salts of sorrel*, are separated. In order to extract the oxalic acid, acetate of lead is poured into a solution of salt of sorrel, when oxalate of lead is precipitated, which is decomposed by sulphuric acid; after which the liquid, on evaporation, yields crystals of oxalic acid  $C_2O_3, HO + 2HO$ .

The greater part of the oxalic acid now in use in laboratories is prepared by the reaction of nitric acid on sugar, (§ 259.)

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appear hydrogen and carbonic acid, resulting from the oxidation of the oxalic acid formed, at the expense of an equivalent of water, whence the hydrogen. Acetic acid is considered as a pairing of oxalic acid  $C_2O_3$  with methyl  $C_2H_6$ , which view is sustained by the decomposition of the acid, ensuing as follows:



Methyl is also formed in the decomposition of iodohydric ether by zinc, in presence of water; and in the decomposition of cyanohydric ether (cyanide of ethyl) by potassium. It is a colourless and inodorous gas, almost insoluble in water, soluble in alcohol, and does not liquefy at  $-0.4^\circ$ . Its specific gravity being 1.037, its formula  $C_2H_6$  corresponds to a condensation to 2 volumes. It should be regarded as  $H(C_2H_2)$ , or hydrogen paired with elayl, or olefant gas.

Combinations of methyl with several metalloids and metals have been discovered, but are not yet fully investigated; the only one which is well known being a compound of arsenic with 2 equivalents of methyl, or *cacodyl*, already described, (§ 1381.)

*Zincmethyl*  $ZnC_2H_5$  or  $Zn, H(C_2H_2)$  and  
*Phosphuretted methyl*  $P, C_2H_5$  or  $P, [H(C_2H_2)]_3$ ,

corresponding to phosphuretted hydrogen have been obtained. Zincmethyl resembles zincethyl; and phosphuretted methyl bears a close analogy to phosphuretted hydrogen.—*W. L. F.*

\* *Oxalis acetosella*, whence the name.—*W. L. F.*

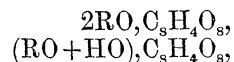
MALIC ACID  $C_5H_4O_6, 2HO$ .

§1447. Malic acid is most widely diffused through the organic kingdom, being found partly free and partly combined with potassa, lime, magnesia, and some organic bases, and giving rise to the acid taste observed in fruits before maturity. Malic acid is generally obtained from the berries of the mountain ash, which are collected before maturity, crushed, and their juice expressed. The juice is clarified by being boiled for a few moments with white of egg and filtered, when acetate of lead is added, which yields a white crystalline precipitate of malate of lead; the salt, however, being always mixed with a small quantity of other organic substances, which are precipitated in combination with the oxide of lead. Malate of lead is nearly insoluble in cold, but readily soluble in boiling water, and is purified by boiling with water the crude malate of lead previously filtered, and rapidly filtering the liquor; when the latter deposits, on cooling, malate of lead in small crystalline spangles. The mother liquid is again boiled with the residue of the first ebullition, and this is continued until the hot liquor no longer deposits malate of lead on cooling. The foreign plumbic compounds remain in the residue.

Crude malate of lead is usually decomposed by sulfhydryc acid, (§1207,) and the impure malic acid is thus isolated; after which the solution of malic acid thus obtained is boiled for a few moments, in order to drive off the sulfhydryc acid, and then divided into two equal parts. One part, which has been accurately saturated with ammonia, is poured into the second part, which remained in the state of free malic acid, which furnishes a solution of bimalate of ammonia, or rather a neutral malate of ammonia and water ( $NH_3, HO + HO$ ),  $C_5H_4O_6$ , which is crystallized; and as the salt crystallizes very readily, it is purified by successive crystallizations. If the malate of lead contained tartrate and citrate of lead, as frequently happens, the first crystals deposited by the solution of impure bimalate of ammonia would be bitartrate of ammonia, which is very slightly soluble; after which the bimalate would crystallize, while the citrate would remain in the mother liquid. In this case, the bimalate of ammonia is again converted into malate of lead, and the salt is again decomposed by sulfhydryc acid.

The solution of malic acid is evaporated to the consistence of syrup, and then left in vacuo, when it deposits colourless crystals of hydrated malic acid,  $C_5H_4O_6, 2HO$ , which are deliquescent, and cannot be freed from their water without decomposition.

Malic acid is a powerful acid, forming a great number of salts, and producing in general, with the same base, two salts, the formulæ of which, when deprived of their water of crystallization, are



and it is therefore a bibasic acid, as we stated in §1225.



Alkaline malates are very soluble and deliquescent, which is equally true of the malate of ammonia  $2(\text{NH}_3, \text{HO}), \text{C}_8\text{H}_4\text{O}_8$ ; while the malate  $(\text{NH}_3, \text{HO} + \text{HO}), \text{C}_8\text{H}_4\text{O}_8$ , on the contrary, crystallizes readily. Malate of lime crystallizes with 6 equivalents of water of crystallization, and presents the formula  $(\text{CaO} + \text{HO}), \text{C}_8\text{H}_4\text{O}_8 + 6\text{HO}$ .

§ 1448. Crystallized malic acid melts at  $181.4^\circ$ , and, if kept for some time at a temperature of  $347^\circ$ , is converted into two new acids, called *maleic* and *paramaleic*, which are isomeric, and present the formulæ  $\text{C}_4\text{HO}_3, \text{HO}$ . Water separates from them, without disengagement of gas. If the retort be rapidly heated to  $392^\circ$ , the maleic acid distils over, with very small quantities of paramaleic acid, for, at this temperature, but a small quantity of the latter acid is formed. Distilled maleic acid solidifies in large crystals in the neck of the retort and the receiver, and is very soluble in water and alcohol, its solution not being clouded by limewater, while water of baryta throws down a white precipitate in crystalline spangles, and acetate of lead produces a similar precipitate. The maleates of potassa and soda crystallize readily. The general formula of the dried maleates is  $\text{RO}, \text{C}_4\text{HO}_3$ , showing maleic acid to be monobasic. Maleic acid has been found in several vegetables, particularly in the horsetail, (*equisetum fluviatile*), whence it has also been called equisetie acid.

If maleic acid be heated to only  $302^\circ$ , and be kept for some time at this temperature, the second acid, or *paramaleic*, is abundantly formed instead of the first. It is much less fusible than maleic acid, for it melts at only about  $390^\circ$ , and sublimes at a higher temperature; and it is moreover easily distinguished from it by being very slightly soluble in water, 200 parts of water dissolving about 1 part of it. Paramaleic acid produces with oxide of silver, a salt remarkable for its insolubility, and yields, with potassa, soda, and ammonia, easily crystallizable salts. It may be boiled with nitric acid without undergoing any change. The general formula of the paramaleates is  $\text{RO}, \text{C}_4\text{HO}_3$ , and that of crystallized paramaleic acid is  $\text{C}_4\text{HO}_3, \text{HO}$ .

Maleic acid is converted into paramaleic acid when it is kept for a long time at a temperature exceeding  $302^\circ$ , while the maleates themselves, heated to  $480^\circ$  or  $570^\circ$ , are converted into paramaleates.

Paramaleic acid is also found in vegetables, and having been obtained from fumitory, (*fumaria officinalis*), has hence been called *fumaric acid*. It has also been found in Iceland moss.

#### CITRIC ACID $\text{C}_6\text{H}_8\text{O}_{11}, 3\text{HO} + 2\text{HO}$ .

§ 1449. Citric acid, which exists in the juice of a large number of acid fruits, particularly in lemons, gooseberries, and currants, is generally extracted from lemons, by allowing their juice to ferment spontaneously for some time, when mucilaginous substances separate from it; after which the liquid is saturated with finely powdered chalk, gradually added, so as not to be in excess, and it is boiled. Citrate of lime, being insoluble, is precipitated, and is de-

composed by a slight excess of sulphuric acid; and the sulphate of lime being then separated by filtering, the acid liquid is carefully evaporated, until a crystalline crust begins to form on its surface, when it is left to itself. Citric acid crystallizes in large crystals, the presence of a slight excess of sulphuric acid assisting the crystallization. The acid is very soluble in water, for it dissolves in  $\frac{1}{2}$  of its weight of cold, and  $\frac{3}{4}$  of its weight of boiling water. After a time, its aqueous solutions become mouldy.

The formula of citric acid crystallized at the ordinary temperature is  $C_{12}H_5O_{11} \cdot 5HO$ , while that of the acid dried at  $212^\circ$  is  $C_{12}H_5O_{11} \cdot 3HO$ , the 3 equivalents of water which remain being basic, and replaceable by equivalent quantities of bases. The formula of citrate of silver is  $3AgO, C_{12}H_5O_{11}$ , and a *methylocitric ether* is known of the formula  $3(C_2H_3O), C_{12}H_5O_{11}$ .

The alkaline citrates are soluble, while those of the alkaline earths and other metallic oxides are generally insoluble, but dissolve in an excess of citric acid.

About 1 per cent. of crystallized citric acid may be obtained from the juice of common currants, by fermenting it with beer-yeast, when the saccharine matter is converted into alcohol, which is separated by distillation; and the residue, being saturated with chalk, yields citrate of lime.

§ 1450. Citric acid is decomposed by heat, carbonic acid being first disengaged, with oxide of carbon and acetone; while at a higher temperature, an oleaginous substance is formed which distils. If the operation be arrested at the moment of the appearance of the oleaginous substance, the residue contains only a very small quantity of unaltered citric acid, and consists almost entirely of a peculiar acid, called *aconitic*, because it was first found in a vegetable, the *aconitum napellus*. The composition of this acid  $C_4HO_3, HO$  is the same as that of maleic acid, and its properties are very analogous, while it appears to differ from it in some of its reactions, and seems therefore to be a second isomeric modification of this acid.

Aconitic acid melts at about  $284^\circ$ , and distils at  $320^\circ$ ; but the product which passes over is no longer aconitic acid, oleaginous drops, which crystallize on cooling, being formed. The same product is necessarily obtained by the direct distillation of citric acid. It dissolves in water, and yields an acid liquid depositing crystals on evaporation, which are purified by being redissolved in alcohol or ether. They are formed by a new acid, which has been called *pyroaconitic* and *itaconic acid*, the formula of which, in the crystallized state, is  $C_5H_2O_5, HO$ , while that of itaconate of silver is  $AgO, C_5H_2O_5$ .

If itaconic acid be again distilled, it is soon found to change, for the oily drops which condense no longer crystallize by cooling, being formed by a new acid, called *citraconic*. The same acid may be obtained by means of the crude product yielded by the imme-

diate distillation of citric acid, for which purpose it suffices to distil it a second time in a retort heated in an oil-bath, and to collect separately the products which distil at a temperature beyond  $392^{\circ}$ . A very fluid, colourless liquid is thus obtained, boiling at  $413^{\circ}$ , and of which the density is 1.247. Its formula being  $C_5H_4O_3$ , its composition is consequently the same as that of anhydrous itaconic acid. Exposed to a moist atmosphere, it slowly absorbs the vapour of water, and is converted into a crystalline compound which melts at about  $176^{\circ}$ , the formula of which is the same as that of crystallized itaconic acid, and their composition is also the same, while itaconic acid melts only at about  $320^{\circ}$ , and the crystallized acid formed by the combination of anhydrous citraconic acid with water melts at  $178^{\circ}$ . The two products are therefore merely isomeric. Hydrated citraconic acid yields, by distillation, anhydrous citraconic acid.

TARTARIC ACID  $C_4H_4O_6, 2HO$ .

§ 1451. Tartaric is one of the most important of the organic acids, and exists in a great number of fruits, such as grapes, pine-apples, mulberries, and other vegetables. On a large scale it is always made from grape-juice, in which it exists in the state of bitartrate of potassa and neutral tartrate of lime, the two salts being in solution; for the first is eminently soluble, and the second, although insoluble in water, dissolves in an acid liquid. When grape-juice is fermented in order to be made into wine, the bitartrate of potassa and tartrate of lime are slowly precipitated, being insoluble in the alcoholic water, and they form a crust which adheres to the sides of the barrel. This crust, called *tartar*, is red or white according to the colour of the wine which produces it, and is mixed with many foreign substances. In order to purify this *crude tartar*, or *argol*, it is powdered, and boiled for several hours with enough water to dissolve it, after which the liquid is then allowed to cool; when, in the course of a few days, crystals form, which adhere to the sides of the vessel, while the residue is composed chiefly of foreign substances. The crystals, being separated, are redissolved in boiling water, while clay and animal black are added, and the boiling liquid is filtered. The latter yields, on cooling, very pure crystals of bitartrate of potassa, which is the *cream of tartar* of commerce.

In order to extract tartaric acid from cream of tartar, it is dissolved in about 10 times its weight of boiling water, and finely powdered chalk is gradually added, until effervescence ceases, when the lime has formed, with one-half of the tartaric acid, an insoluble tartrate of lime, while the other half of the tartaric acid remains in the liquid in the state of neutral tartrate of potassa. A solution of chloride of calcium is then added, until no more precipitate is thrown down, when the remainder of the tartaric acid is thus separated in the state of tartrate of lime. The two portions of tartrate of lime are united and decomposed by sulphuric acid diluted with

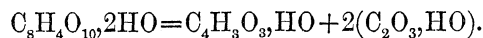
3 or 4 times its weight of water, 52 parts of concentrated sulphuric acid being usually taken for 100 parts of cream of tartar, which is a little more than is absolutely necessary to decompose the tartrate of lime. The sulphate of lime being separated by filtering, the acid liquid, evaporated to the consistence of syrup, is then left to itself, in a slightly warm situation to prevent it from becoming too viscous; when it yields beautiful crystals, which are purified by a second crystallization. The acid is largely used in dyeing.

Tartaric acid, dissolved in water, exerts rotation to the right, with a specific energy the greater as the proportion of water is larger and the temperature higher. It then divides the planes of polarization of the various simple rays according to the laws peculiar to it, and in which it differs from all known substances. These laws are modified, without losing their peculiarity, when it is dissolved in alcohol or wood-spirit, but disappear completely when it is brought into the presence of alkaline bases or boracic acid, when the phenomena reassume the appearance common to the generality of substances possessing a rotatory power.

Tartaric acid is obtained in large and generally well-defined crystals, of the density 1.75. Boiling water dissolves about twice its weight of it, and cold water a little more than its own weight, while alcohol dissolves it more sparingly. The composition of crystallized tartaric acid corresponds to the formula  $C_8H_6O_{12}$ , which is commonly written  $C_8H_4O_{10}, 2HO$ . The two equivalents of water cannot be driven off by heat without injury to the acid, and in the anhydrous tartrates they are replaced by 2 equivalents of the base. The same base generally forms two salts with tartaric acid; the formula of the first, called *neutral tartrate*, being  $2RO, C_8H_4O_{10}$ , while that of the second, or *bitartrate*, is  $(RO + HO), C_8H_4O_{10}$ .

These denominations are very erroneous, since the salts, from their constitution, are both neutral, and because, in both cases, the acid is saturated by 2 equivalents of base; with the difference that in the second case, one of the equivalents of base, water, does not saturate the acid as regards its reaction on vegetable colours.

From its composition, tartaric acid may be regarded as formed of 1 equiv. of acetic acid and 2 equiv. of oxalic acid, and we have, in fact,



It is actually decomposed in this manner, when heated with alkalis in excess, at a temperature of  $302^\circ$ .

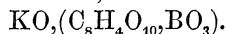
It is a powerful acid, and dissolves several metals with disengagement of hydrogen, particularly zinc and iron. It is decomposed by several easily reducible metallic oxides: thus, at the boiling point, peroxide of lead decomposes it into carbonic acid, water, and formic acid; the liquid, on cooling, depositing very pure crystals of formiate of lead.

The soluble neutral tartrates generally become less soluble by

the addition of an excess of acid, while the insoluble neutral tartrates dissolve, on the contrary, in an excess of acid.

§ 1452. Potassa forms 2 tartrates: the *neutral*, or rather *bi-potassic tartrate*  $2\text{KO}, \text{C}_8\text{H}_4\text{O}_{10} + 2\text{HO}$ , which dissolves in its own weight of water, and loses by heat its equivalents of water of crystallization, and the *bitartrate*, or rather the *monopotassic tartrate*  $(\text{KO} + \text{HO}), \text{C}_8\text{H}_4\text{O}_{10}$ , which is cream of tartar. This salt requires for its solution 18 parts of boiling and more than 200 of cold water, and it is nearly insoluble in alcohol at 0.85. Its crystals, which are hard and opaque, are decomposed by heat, and yield a mixture of carbonate of potassa and charcoal, or *black flux*, (§ 438.)

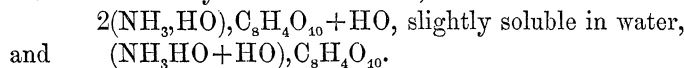
Bitartrate of potassa forms a compound with boracic acid, called *soluble cream of tartar*, which is generally prepared by dissolving in boiling water  $47\frac{1}{2}$  parts of cream of tartar and  $15\frac{1}{2}$  parts of crystallized boracic acid. The liquor, when evaporated, leaves a non-crystalline white mass, insoluble in alcohol, but which dissolves in  $1\frac{1}{2}$  part of cold water, or in  $\frac{1}{2}$  part of boiling water. The formula of this substance, dried at  $212^\circ$ , is



At  $545^\circ$  it loses 2 equiv. of water, becoming  $\text{KO}(\text{C}_8\text{H}_2\text{O}_8, \text{BO}_3)$ , and the organic compound which it then contains presents no longer the composition which we have assigned to anhydrous tartaric acid, although when redissolved in hot water it reproduces the original substance.

Soda also forms two tartrates,  $2\text{NaO}, \text{C}_8\text{H}_4\text{O}_{10} + 4\text{HO}$ , which readily parts with its water in a dry vacuum, and  $(\text{NaO} + \text{HO}), \text{C}_8\text{H}_4\text{O}_{10}$ .

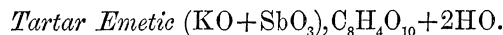
Ammonia also yields two tartrates, of which the formulæ are



Lime forms 2 tartrates: the neutral salt  $2\text{CaO}, \text{C}_8\text{H}_4\text{O}_{10} + 8\text{HO}$ , which is nearly insoluble in cold water, and is frequently found in beautiful crystals in crude tartar, and the acid tartrate  $(\text{CaO} + \text{HO}), \text{C}_8\text{H}_4\text{O}_{10}$ .

By saturating cream of tartar with carbonate of soda and crystallizing it, a double tartrate of potassa and soda is obtained  $(\text{KO} + \text{NaO}), \text{C}_8\text{H}_4\text{O}_{10} + 8\text{HO}$ , called *Rochelle salt*, which is used in medicine, and is generally prepared by dissolving in boiling water 1 part of crystallized carbonate of soda and  $1\frac{1}{2}$  part of cream of tartar, when the salt is obtained in large prismatic crystals.

All the tartrates, when dissolved in water, exert rotation to the right, while tartrate of lime, dissolved in chlorohydric acid, turns the plane of polarization to the left.



§ 1453. Tartar emetic, one of the most valuable medicines used, is a double tartrate of potassa and oxide of antimony, according to the formula  $(\text{KO} + \text{SbO}_3), \text{C}_8\text{H}_4\text{O}_{10} + 2\text{HO}$ . It is prepared by boil-

ing in 5 or 6 parts of water equal parts of oxide of antimony and cream of tartar, and then glass of antimony; the oxychloride or subsulphate may be substituted for the oxide. The hot solution, when filtered, deposits colourless crystals, soluble in 2 parts of boiling and 14 of cold water, which, when heated to  $212^{\circ}$ , part with their 2 equiv. of water of crystallization, while, if heated to  $442.4^{\circ}$ , they lose 2 more equiv., and the remaining product  $(\text{KO} + \text{SbO}_3)$ ,  $\text{C}_8\text{H}_2\text{O}_8$  no longer presents the formula of the tartrates, although if it be redissolved in water it reproduces, by crystallization, the original salt, tartar emetic.

Acids decompose solutions of tartar emetic, bitartrate of potassa and a basic salt of oxide of antimony being separated. Alkalies and the alkaline earths also decompose them, but this precipitate is frequently not formed for some time, as is the case in potassa and soda; by using an excess of which bases no precipitate is formed, because the oxide of antimony remains dissolved in the alkaline liquid. Ammonia and limewater immediately effect a precipitate.

Sulphydic acid decomposes the solution of tartar emetic, and an orange-coloured precipitate of sulphide of antimony is formed. Tartar emetic is decomposed by heat, and, when calcined in a close vessel, yields a residue of antimoniuret of potassium, (§ 1017,) while in Marsh's apparatus it produces abundantly antimonial deposits, (§ 1016.)

By dissolving in boiling water 9 parts of tartar emetic and 4 parts of tartaric acid, evaporating the solution by a gentle heat, and then leaving it to itself, crystals of tartar emetic first separate, and then, by continuing the evaporation, a crystalline compound, efflorescent and very soluble in water, is deposited, the formula of which is  $(\text{KO} + \text{SbO}_3), 2\text{C}_8\text{H}_4\text{O}_{10} + 7\text{HO}$ , corresponding to that of a neutral tartrate. Tartar emetic can also combine with 3 equiv. of bitartrate of potassa, which compound is obtained by dissolving together 10 parts of tartar emetic and 15 of cream of tartar.

Lastly, by pouring into a solution of tartar emetic nitrate of silver or acetate of lead, precipitates are obtained which are species of tartars emetic, in which the oxides of silver or lead replace the potassa. Their formulæ are  $(\text{AgO} + \text{SbO}_3), \text{C}_8\text{H}_4\text{O}_{10}$  and  $(\text{PbO} + \text{SbO}_3), \text{C}_8\text{H}_4\text{O}_{10}$ , etc. etc.; and, like tartar emetic, they lose 2 equiv. of water at a high temperature.

#### *Modifications of Tartaric Acid by Heat.*

§ 1454. When tartaric acid is rapidly heated in an oil-bath to the temperature of  $338^{\circ}$ , it fuses without losing any water, while its composition is remarkably modified; for when redissolved in water and combined with the various bases, it yields salts which differ in their forms and solubility from the ordinary tartrates. The name of *metatartaric* has been given to this modified tartaric acid. The bimetatartarate of ammonia  $(\text{NH}_3\text{HO} + \text{HO}), \text{C}_8\text{H}_4\text{O}_{10}$  is much more

VOL. II.—3 A

soluble than the bitartrate, and produces crystals of a totally different form, and the former salt does not precipitate a solution of chloride of calcium, while the bitartrate does. Boiling converts metatartrates into bitartrates.

By maintaining melted tartaric acid for a long time at a temperature of  $338^{\circ}$  it undergoes a second isomeric modification, and forms an acid called *isotartaric acid*, which, while exhibiting the same composition as tartaric acid, appears to differ from it by saturating only 1 equiv. of base. Isotartrate of lime  $(\text{CaO} + \text{HO})\text{C}_4\text{H}_4\text{O}_{10}$  dissolves readily in cold water, producing a solution behaving perfectly neutral with litmus paper, which, when boiled, becomes acid and deposits crystals of neutral metatartrate of lime. Isotartrate of ammonia is a deliquescent salt, easily converted by heat into the bimetatartrate.

By heating tartaric acid rapidly to  $356^{\circ}$ , it first melts, swells up, loses 12 per cent. of water, and finally solidifies again, forming a substance of the formula  $\text{C}_4\text{H}_4\text{O}_{10}$ , which has become insoluble in water, and may be easily separated by washing from the portions which have not yet undergone the transformation. This substance, which has been called *anhydrous tartaric acid* because it presents the composition of the acid in the anhydrous tartrates, is equally insoluble in alcohol and ether; while, when in contact with water, it is converted successively into the preceding modifications of tartaric acid, the transformation being very rapid in contact with boiling water and the bases.

§ 1455. By heating tartaric acid to distillation, it undergoes a decomposition which produces two new pyrogenated acids, which have been called *pyroracemic* and *pyrotartaric acid*.

Pyroracemic acid is chiefly formed when tartaric acid is rapidly distilled at a temperature of  $428^{\circ}$ . The product, subjected to a second distillation, yields a very acid liquid, consisting of a mixture of pyroracemic and acetic acids, which, when saturated with carbonate of lead, forms soluble acetate of lead, while the pyroracemate of lead remains in the shape of an insoluble precipitate. The precipitate is rapidly washed in cold water, suspended in water, and decomposed by a current of sulphydric acid gas, and the acid solution, when evaporated, is reduced to a syrupy condition without crystallizing. Pyroracemic acid forms a great number of salts; the pyroracemate of potassa is deliquescent, while that of soda crystallizes readily, and the salts of lime and baryta are soluble in water. Pyroracemate of silver is obtained by double decomposition, and separates in small crystalline spangles of the formula  $\text{AgO}, \text{C}_6\text{H}_3\text{O}_8$ , showing the formula of anhydrous pyroracemic acid as it exists in dry salts to be  $\text{C}_6\text{H}_3\text{O}_8$ . The name given to this acid is very improper, for it seems to indicate that pyroracemic acid is a special pyrogenated product of racemic acid, which is presently to be described.

If tartaric acid be rapidly heated to about  $570^{\circ}$  the products of its decomposition differ from those just indicated, and the receiver contains a brown liquid, which is subjected to a second distillation. The first products are collected separately, and the receiver changed when the substance in the retort becomes syrupy. The liquid which then distils sets into a crystalline mass under the receiver of an air-pump, and the crystals are pressed between several folds of tissue-paper, in order to free them from adherent empyreumatic matter, redissolved in water, and, after having discoloured the solution by boiling it with a small quantity of animal black, it is again evaporated, and yields crystals of pure *pyrotartaric acid*. A much larger proportion of pyrotartaric acid is prepared by subjecting to the action of heat an intimate mixture of tartaric acid and platinum-sponge, or even of powdered pumice-stone, the latter substance assisting the decomposition, which then takes place at a lower temperature. Pyrotartaric acid melts at about  $212^{\circ}$ , and distils at  $356^{\circ}$ , while a portion of it is decomposed. It is very soluble in water and alcohol, and its solutions are not precipitated by baryta or lime-water. Pyrotartaric acid is probably a monobasic acid, of which the formula, in anhydrous salts, is  $C_5H_3O_3$ ,

PARATARTARIC, RACEMIC, OR UVIC ACID  $C_6H_4O_{10}, 2HO + HO$ .

§ 1456. The acid to which these various names have been given, has only been obtained once, accidentally, in making tartaric acid on a large scale, and never has been since produced. We shall retain the name of *racemic acid* alone. The composition of racemic acid, when dried, is exactly the same as that of tartaric acid, and the composition of the salts it forms with the different bases is also identical with those of the corresponding tartrates, the two acids exhibiting one of the most remarkable examples of isomerism, but crystallized racemic acid contains 1 equivalent of water more than tartaric acid, which is easily driven off by heat. Racemic acid differs from tartaric acid in the crystalline form and solubility of its salts, and also in its physical properties, particularly in the absence of all rotatory action on the plane of polarization. But we shall soon see that this neutrality is owing to its being the union, in equal weights, of two acids, one of which is tartaric acid itself, and the other an acid which differs from it only by an opposition of hemihedrism in crystalline forms, and by an equally identical rotatory power, but in an opposite direction. Nevertheless, for the moment, we shall continue to describe the properties of racemic acid as though it were simple, in order to conform to the language adopted.

Racemic is much less soluble in water than tartaric acid, and as it only dissolves in 5.7 parts of cold water, it is easily separated from the latter acid by crystallization. The two acids are also dis-



tinguished by the manner in which they behave with limewater: thus, tartaric acid does not form immediately any precipitate in lime water, and a crystalline deposit is not thrown down until after some time, while racemic acid immediately affords a white precipitate. By dissolving separately in weak chlorohydric acid, tartrate and racemate of lime, and carefully saturating the two liquids with ammonia, the racemate of lime is immediately precipitated in an opaque crystalline powder, while the tartrate of lime, on the contrary, is slowly deposited in the form of small transparent crystals.

Like tartaric acid, racemic acid is a bibasic acid, and forms two salts with potassa, one  $(\text{KO} + \text{HO})\text{C}_8\text{H}_4\text{O}_{10}$  corresponding to cream of tartar, and even less soluble than that tartrate, while the other  $2\text{KO}, \text{C}_8\text{H}_4\text{O}_{10}$  is very soluble.

Ammonia yields two salts:  $(\text{NH}_3, \text{HO} + \text{HO})\text{C}_8\text{H}_4\text{O}_{10}$ , which only dissolves in 100 parts of water; and  $2(\text{NH}_3, \text{HO})\text{C}_8\text{H}_4\text{O}_{10}$ , which is very soluble, and affords beautiful crystals.

The salt of soda  $(\text{NaO} + \text{HO})\text{C}_8\text{H}_4\text{O}_{10} + 2\text{HO}$  dissolves in 12 parts of water, while the salt  $2\text{NaO}, \text{C}_8\text{H}_4\text{O}_{10}$  is much more soluble.

Racemic, like tartaric acid, forms crystallizable double salts, and produces, with potassa and soda, a double racemate, having the same composition as Rochelle salt, but differing from it in its crystalline form and in its solubility.

Subjected to the action of heat, racemic acid appears to afford the same modifications as tartaric acid, and pyrogenated acids identical with those produced by the latter substance.

#### *Dextro-racemic and Levo-racemic Acid.*

§ 1457. The solution of the neutral racemates of soda, potassa, or ammonia, and even that of a double racemate of potassa and antimony, exert no rotatory power, and if they be allowed to evaporate spontaneously, the form and all the other physical properties of the crystals progressively precipitated are identical in each, and they are merely distinguished from each other by their size.

Such is not the case with double racemates of soda and ammonia, or of soda and potassa. Their solutions are still deprived of rotatory power, but the crystals deposited by each are of two kinds, distinguished from each other by hemihedral facets in opposite directions. If they are separated according to this character, and each sort dissolved by itself, two solutions are obtained possessing equal and inverse rotatory powers, so that if they are mixed together in equal quantity, the resulting rotatory power is null, like that of the original solution before the separation.

As a single sorting, by hand, is never strictly exact, separation may be effected more perfectly by redissolving each sort of crystal separately, and rejecting the first which are deposited. Those sub-

sequently obtained are generally formed alone, and of a single sort, thus completing the separation.

The acid peculiar to each sort of crystal is extracted from its salts in a similar manner as tartaric acid is extracted from the tartrates. One of the acids exerts rotation toward the right, like tartaric acid, and with the same special characters of dispersion; and while its chemical composition is the same, it also behaves exactly like it in the presence of boracic acid and the alkaline bases, producing crystals of exactly the same form. In short, nothing distinguishes it from ordinary tartaric acid; but it is nevertheless, called *dextro-racemic acid*, in order to recall its origin, and to not decide too hastily on its density.

The other acid, extracted from crystals of the opposite form, is identical with tartaric acid in its ponderable composition, but exactly inverse in its rotatory properties. They are exerted toward the left, as those of tartaric acid toward the right, with the same energy, the same laws of dispersion, and evincing similar reactions in the presence of the same substances. It has been called *levo-racemic acid*, and it crystallizes in the same form as tartaric acid, except that its crystals have hemihedral facets in opposite directions.

Levo-racemic and dextro-racemic acid being dissolved together in equal weights, combine immediately, and reproduce racemic acid, the mixed solution becoming neutral in polarized light, and the crystals deposited by it exhibiting no distinctive characters. The individual dissymmetry of the two compounds has disappeared in their union, and when combined they are identical with racemic acid which has not been decomposed.

## TANNIC ACIDS.

§ 1458. The name of *tannin* has been given to several substances, probably of different composition, which possess the property of forming insoluble compounds with albumen, gluten, gelatin, fibrin, the animal tissues in general, and the epidermis and skin of animals. These compounds will not putrefy, and are unchangeable by water; on which properties is founded the process of tanning of skins, to be described at the close of this work. Tannins exist in almost all vegetables, in the bark and leaves of trees, and the seeds of fruits; the oak, chestnut, elm, and willow containing large quantities of it, while it occurs most abundantly in galls, a sort of excrescence which grows on the leaves of the oak when they have been punctured by a certain insect.

In order to extract tannin, the galls are finely powdered and introduced into a displacer, (fig. 683,) the neck of which has been previously stopped with a plug of cotton, the powder being heaped upon it, and ordinary ether of commerce poured



Fig. 688.

on. The tube is corked, and adjusted in a flask, as represented in the figure; when the ether filters slowly through the galls, while the tannin contained in the latter dissolves in the water given off by the ether, a very small portion being dissolved by the ether itself. The liquid which falls into the flask divides into two layers, the inferior stratum, of the consistence of syrup and colour of amber, being a highly concentrated aqueous solution of tannin, while the upper layer is ether, holding in solution a small quantity of tannin and some other substances extracted from the galls. The ether is again poured upon galls, in order to abstract an additional portion of tannin; and the aqueous solution of tannin is shaken several times with pure ether, and then evaporated under the receiver of an air-pump, when a spongy mass, without any appearance of crystallization, generally slightly yellowish, remains, consisting of tannin in its greatest state of purity known. It is a spongy, brilliant, very light, generally yellowish substance, but sometimes is obtained of a perfectly white colour. It dissolves freely in water, and gives it a strongly astringent taste; and as it reddens litmus and decomposes the carbonates, it is often called tannic acid. Tannin combines with bases, and precipitates the majority of the metallic solutions, the colours of the precipitates being frequently characteristic; whence tannin and an infusion of galls are often used as tests to distinguish various metals from each other. The composition of tannin dried at  $248^{\circ}$  corresponds to the formula  $C_{18}H_8O_{12}$ , which should probably be written  $C_{18}H_5O_9 \cdot 3H_2O$ ; for, on pouring a solution of tannin into a boiling solution of acetate of lead and maintaining ebullition for some time, a yellow precipitate of the formula  $3PbO, C_{18}H_5O_9$  is formed.

Tannin yields a deep-blue precipitate with sesquisalts of iron, which compound is very important, being the colouring principle of ordinary writing-ink. In order to prepare ink,  $1\frac{1}{2}$  part of powdered galls are boiled for 3 hours with 15 of water, filling up the water as it evaporates; after which the liquid is filtered, and 2 parts of gum and 1 part of protosulphate of iron are added, besides frequently a small quantity of a solution of copper. The mixture is frequently shaken, and exposed in open vessels, in order that the protoxide of iron may absorb oxygen from the air and be converted into sesquioxide, which causes the colour of the liquid, at first brown, gradually to deepen and become bluish black. Oxidation being arrested at the proper shade, the ink is bottled. This kind of ink contains a large amount of protoxide of iron, at the moment of using it, and the marks which it leaves on paper, being at first pale, turn black when they have absorbed the oxygen necessary for the peroxidation of the iron.

Tannin completely precipitates gelatin and albuminous substances

from their solutions; and animal membranes and skins, dipped into a solution of tannin, ultimately abstract all this substance which is incorporated in the membrane, thus rendering it unchangeable and imputrefiable.

Tannin combines also with a large number of the mineral acids, and forms ill-defined compounds, soluble in pure water, but very slightly so in an excess of acid.

*Gallic Acid*  $C_7H_5O_5, HO$ .

1459. Gallic acid is always prepared from tannin or galls, and several processes may be adopted.

1. By causing sulphuric or chlorohydric acid, diluted with 8 or 10 times their weight of water, to act on tannin, and boiling the mixture for about 12 hours, taking care to fill up the water as it evaporates, the tannin is almost wholly converted into gallic acid, the greater portion of which crystallizes during the cooling of the liquid.

2. By exhausting powdered galls with cold water, concentrating the filtered liquid by evaporation, and saturating it exactly with caustic potassa. Chlorohydric acid is added to the liquid when cooled, when a deposit of brown crystals of impure gallic acid is precipitated, which is dissolved in boiling water; and the hot solution being left for some time in contact with animal black, which removes the colouring matter, the filtered liquid is allowed to cool, when the gallic acid crystallizes in a state of purity.

3. The process usually employed in the preparation of gallic acid is founded on a peculiar and spontaneous fermentation experienced by galls, and by which its tannin is converted into gallic acid. Moistened and powdered galls are left for several months at a temperature of  $68^{\circ}$  to  $86^{\circ}$ , in an earthen vessel, when the substance becomes covered with small whitish crystals of gallic acid. Toward the close, the substance is allowed to dry, and is treated with boiling alcohol, which dissolves the gallic acid alone, and deposits the greater portion of it on cooling. If an extract of galls be substituted for the galls, the transformation of the tannin takes place in the same way, though more slowly; while if a solution of pure tannin be used, the transformation does not ensue. We are hence naturally led to infer that galls contain substances which induce the conversion of tannin into gallic acid, and which behave like ferments, since the transformation is arrested by all substances which destroy the fermentation of the yeast. The presence of air does not appear to be necessary, because gallic fermentation of extract of galls takes place even in an hermetically closed vessel.

Gallic acid crystallizes in long silky aciculæ, which are sometimes perfectly white, but more frequently slightly yellowish; and it is deposited in larger prismatic crystals from an alcoholic or etherial solution. It dissolves in 100 parts of cold and in 3 only

of boiling water; and it neither precipitates gelatin nor attaches itself to animal membranes; thus furnishing a ready method of separating it from tannin.

The formula of crystallized gallic acid is  $C_7H_3O_5 \cdot HO$ , and it loses 1 equivalent of water at  $212^\circ$ . The acid forms a large number of salts, the composition of which has not yet been sufficiently studied; and therefore chemists are not agreed upon the formula for anhydrous gallic acid.

By dropping an alcoholic solution of potassa into an alcoholic solution of gallic acid, until perfect saturation is effected, white flakes of a salt of the formula  $KO, 3(C_7H_3O_5)$  are deposited; while an excess of potassa decomposes the gallic acid.

By exactly saturating a solution of gallic acid with ammonia, a salt is obtained by evaporation, of which the composition corresponds to the formula  $(NH_3, HO), 2C_7H_3O_5 + HO$ ; while, if only one-half of the ammonia necessary to saturation be added, there results a compound, slightly soluble when cold, and corresponding to the formula  $(NH_3, HO), C_7H_3O_5 + C_7H_3O_5$ .

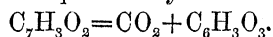
The gallate of lead, which is precipitated by pouring a solution of gallic acid into a boiling solution of acetate of lead in excess, forms white flakes, which change, by heat, into yellowish crystalline granules, corresponding to the formula  $2PbO, C_7H_3O_5$ .

It therefore frequently occurs in the gallates, that the acid in combination with the base presents the formula  $C_7H_3O_5$ , which would seem to indicate that such is the composition of anhydrous gallic acid, and that crystallized gallic acid should be written  $C_7H_3O_5, 2HO + HO$ ; one of the equivalents of water being water of crystallization, while the other two are basic.

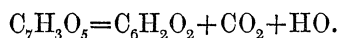
The aqueous solution of gallic acid remains unchanged in well-closed vessels, but soon becomes mouldy in the air. Gallic acid dissolves in concentrated hot sulphuric acid, forming a red liquid, which, when poured into cold water, yields a red crystalline precipitate of the formula  $C_7H_2O_4$ ; which new compound differs from crystallized gallic acid only in the loss of 2 equivalents of water.

A solution of gallic acid colours sesquisalts of iron of a deep blue; and when the liquid is concentrated, a precipitate of the same colour is formed. Gallic acid precipitates several metals from their solutions, particularly silver and gold, which reduction is more easily effected in the light of the sun.

§1460. By heating gallic acid in a retort over an oil-bath, it first loses 1 equivalent of water, and then melts, and if the temperature be raised to  $365^\circ$ , and kept stationary for some time at this point, carbonic acid is disengaged, while a pyrogenated acid, *pyrogallie acid*  $C_6H_3O_3$ , sublimes in white crystalline spangles, only a small brown residue being left in the retort. The reaction which produces pyrogallie acid is expressed by the following equation:



If, on the contrary, the temperature be suddenly raised to  $460^{\circ}$  or  $480^{\circ}$ , water and carbonic acid are both disengaged, and a small quantity of pyrogallic acid still sublimes, while the greater portion of the gallic acid is converted into a brown substance, which remains in the retort. In its appearance and chemical properties, this acid closely resembles humic and ulmic acids, (§ 1307,) being insoluble in water, but dissolving in alkaline liquids and forming brown solutions, from which acids precipitate the original substance unchanged. This substance has been called *metagallic acid*, and its composition corresponds to the formula  $C_6H_2O_2$ ; the reaction by which it is derived from gallic acid being expressed by the equation,



Pyrogallic acid may be prepared by carefully heating powdered galls, or still better, its evaporated extract, in an earthen vessel covered with a pasteboard cone, when crystals of the acid sublime on the sides of the cone. Pyrogallic acid, which is very soluble in water, alcohol, and ether, melts at  $257^{\circ}$ , sublimes at about  $410^{\circ}$ , and is decomposed at  $482^{\circ}$  into water and metagallic acid. It turns salts of the protoxide of iron of a deep blue colour, and those of the sesquioxide of an intense red.

*Ellagic Acid*  $C_{14}H_2O_7, HO$ .

§ 1461. Extract of galls, exposed for a long time to the air, contains, in addition to gallic acid, another acid, insoluble in water, and to which the name of *ellagic* has been given. This latter acid is extracted from the deposit formed at the bottom of the vessel, by treating it first with boiling water which dissolves the gallic acid, and then with a solution of potassa which dissolves the gallic acid in the state of ellagate of potassa. The alkaline liquid, when evaporated, deposits the latter salt in the form of small crystalline spangles, insoluble in fresh water, but dissolving readily in an alkaline liquid. Acids separate ellagic acid in the form of a slightly yellowish powder.

Ellagic acid is insoluble in water, alcohol, and ether, and its composition corresponds to the formula  $C_{14}H_5O_{10}$ . It loses 2 equivalents of water at  $248^{\circ}$ , when its formula becomes  $C_{14}H_3O_8$ . The formula of ellagic acid in combination with bases being  $C_{13}H_2O_7$ , that of the dried acid is therefore  $C_{14}O_2H_7, HO$ , and that of the hydrated acid  $C_{14}H_2O_7, HO + 2HO$ .

Ellagic acid also occurs in the animal economy, sometimes forming concretions known by the name of *bezoars*.

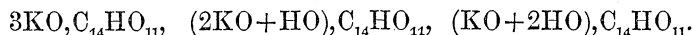
*Meconic Acid*  $C_{14}HO_{11}, 3HO$ .

§ 1462. Meconic acid is extracted from opium. When chloride

of calcium is poured into an infusion of opium, a precipitate of impure meconate of lime is formed, which, after being washed successively with water and alcohol, is treated with 20 parts of hot water, to which 3 parts of chlorohydric acid are added, when the filtered liquid deposits, on cooling, acid meconate of lime. The salt is digested with the same quantity of hot acidulated water, and, on cooling, the meconic acid separates; but it is generally necessary to repeat this operation once or twice before obtaining the acid entirely free from lime. The impure meconic acid may also be combined with potassa, and the meconate of potassa decomposed by chlorohydric acid, after being purified by crystallization.

Meconic acid dissolves in 4 parts of boiling water, from which it is almost wholly deposited, on cooling, in the form of crystalline, pearly white spangles. It is decomposed by long boiling with water, particularly in the presence of chlorohydric acid; carbonic acid being disengaged, while a new acid, called *comenic*, is formed. It is also destroyed by contact with alkaline liquids, yielding complicated products.

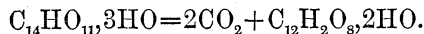
The composition of crystallized meconic acid is represented by  $C_{14}H_{10}O_{20}$ , which formula should be written  $C_{14}HO_{11}, 3HO + 6HO$ , because the 6 equivalents of water of crystallization are driven off at  $212^\circ$ , while the 3 equivalents of basic water may be replaced, either wholly or partly, by bases. In fact, the three following meconates of potassa have been obtained:



By pouring nitrate of silver into a solution of meconate of ammonia, a yellow precipitate of the formula  $3AgO, C_{14}HO_{11}$  is formed.

Meconic acid presents therefore all the characters of a tribasic acid. It produces a beautiful red colour with sesquisalts of iron.

§ 1463. By boiling meconic acid for some time with acidulated water, it is converted into comenic acid, while carbonic acid is disengaged. The formula of comenic acid, is  $C_{12}H_2O_8, 2HO$ , the 2 equivalents of water being basic, for the formula of comenate of silver is  $2AgO, C_{12}H_2O_8$ . Meconic, by being converted into comenic acid, loses only carbonic acid, according to the equation



Comenic acid is also largely formed in the dry distillation of meconic acid, but it is then mixed with another acid, *pyromeconic*, into which comenic acid itself is transformed when subjected to another distillation. In order to obtain pure pyromeconic acid, it must be distilled several times; and the formula of the crystallized acid is  $C_{10}H_3O_5, HO$ , while that of pyromeconate of lead is  $PbO, C_{10}H_3O_5$ . The following equation shows how this acid is derived from comenic acid:  $C_{12}H_2O_8, 2HO = 2CO_2, C_{10}H_3O_5, HO$ .

Comenic and pyrocomenic acids turn sesquisalts of iron of a red colour.

CHELIDONIC ACID  $C_{14}H_{10}O_{10}, 2HO$ .

§ 1464. In celandine, (*chelidonium majus*), a plant of the family of the papaveraceæ, there is formed a peculiar acid, called *chelidonic*, which is there combined with lime; besides malic and fumaric acids. The juice of the plant is expressed and boiled to coagulate the albuminous substances, when, after having added a small quantity of nitric acid, acetate of lead is poured in until a precipitate no longer forms. The chelidonate of lead is alone precipitated, the malic and fumaric acids remaining in solution on account of the excess of nitric acid. The chelidonate of lead, which is mixed with chelidonate of lime, is decomposed by sulphydric acid, and the acid liquor is saturated with lime; after which the chelidonate of lime is crystallized several times. The salt is subsequently decomposed by carbonate of ammonia, and the chelidonate of ammonia resulting, by chlorohydric acid; when the chelidonic acid separates in long crystalline aciculæ during the cooling of the liquid.

The formula of crystallized chelidonic acid is  $C_{14}H_2O_{10} + 5HO$ , and it loses 3 equivalents of water at  $212^\circ$ . From the composition of its salts it should be regarded as a bibasic acid

QUINIC ACID  $C_{14}H_{11}O_{11}, HO$ .

§ 1465. This acid is found in cinchona bark, in the state of quinate of lime. The bark is boiled with water acidulated with chlorohydric acid, which is then saturated with lime, in excess; when the filtered liquid contains quinate of lime which may be crystallized by proper evaporation. The salt is purified by animal black and several successive crystallizations; and in order to separate the quinic acid from it,  $6\frac{1}{2}$  parts of the quinate of lime are heated with 1 of sulphuric acid diluted with 10 of water, when the lime separates in the state of sulphate of lime; after which alcohol is added to effect its complete precipitation, and the filtered liquid is evaporated to the consistence of syrup, when the quinic acid crystallizes in large prisms. The formula of the crystallized acid is  $C_{14}H_{11}O_{11}, HO$ ; and that of quinate of silver is  $AgO, C_{14}H_{11}O_{11}$ .

Quinic acid, subjected to heat, yields very complex products: they are benzin, benzoic phenic, and salicylous acids, all of which shall subsequently be described; besides a peculiar crystallizable substance of the formula  $C_{24}H_{12}O_8$ , very soluble in water and alcohol, and which has been called *hydroquinone*. Subjected to the action of sulphuric acid and peroxide of manganese, quinic acid yields a volatile product, *quinone*, of which the formula is  $C_{24}H_8O_8$ . In order to obtain a small quantity of this product, 100 gm. of quinic acid are heated gently in a small retort with 400 gm. of peroxide of manganese and 100 gm. of sulphuric acid previously diluted



with one-half of its weight of water. A great bubbling ensues in the retort, and a mixture of formic acid and quinone is deposited in the receiver. The latter substance crystallizes in beautiful golden-yellow spangles.

Quinon is easily sublimed by the same method as camphor, and it has a strong and irritating odour, resembling that of camphor. It dissolves slightly in cold, but more freely in boiling water, while its true solvents are alcohol and ether. Chlorine acts powerfully upon it, and gradually abstracts all its hydrogen, which is replaced by an equivalent quantity of chlorine; and two crystallized chlorinated products have thus been separated: *sechlorinated quinone*  $C_{24}H_2Cl_6O_8$  and *perchlorinated quinone*  $C_{24}Cl_8O_8$ .

Quinone also gives rise to a great number of interesting products, but their study would lead us too far.

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§ 1466. Vegetables contain several other organic acids, named generally after the plant from which they are extracted, but they are as yet only imperfectly known; and several of them are probably identical with those already described, for which reason we shall not stop to mention them.

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## ORGANIC ALKALIES.

§ 1467. At the present day a large number of organic substances are known which combine with acids after the manner of mineral bases, forming compounds which exhibit all the characters of salts, and to which the name of *organic alkalies*, or *alkaloids*, has been given. Some are found already formed in vegetables, while others are produced by the calcination or other appropriate treatment of organic matter. The majority of native alkaloids are extremely poisonous, and rank among the most powerful medicines, which character lends them peculiar importance.

All the organic alkalies contain nitrogen and hydrogen, and all, with the exception of ammonia, contain carbon; while the majority, in addition, contain oxygen; and lastly, sulphur has been found in some. They all present the remarkable peculiarity which has been described (§ 513) in treating of ammonia; that of combining directly and without decomposition, with the hydracids, by forming chlorohydrates, iodohydrates, etc. etc., and of fixing, in all salts which they form with the oxacids, 1 equiv. of water, necessary to the constitution of the salt, and which cannot be driven off without destroying its nature. The alkaloids, like ammonia, are therefore bases only when they have combined with the elements of 1 equiv. of water.

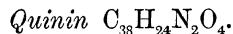
We shall first describe the alkaloids which exist ready formed in vegetables, and then some of the numerous artificial alkaloids obtained in modern days, confining ourselves chiefly to general remarks on the method of their preparation and their properties.

The native alkaloids may be divided into two classes: alkaloids volatile without decomposition, and non-volatile alkaloids, each class requiring a special method of extraction. In order to extract those of the first class, the liquid containing them is distilled with potassa or lime, which bases unite with the acid until then combined with the alkaloid, while the latter passes over in distillation. The majority of non-volatile alkaloids are very slightly soluble in water, and are prepared by boiling the vegetables containing them with water acidulated with chlorohydric acid, when the alkaloid is dissolved in the state of chlorohydrate, after which the liquid is then saturated with an alkali or with lime, in order to precipitate the alkaloid. The deposit is then treated with boiling alcohol to dissolve the alkaloid, which crystallizes on cooling or by evaporation.

#### NON-VOLATILE NATIVE ALKALOIDS.

##### ALKALOIDS OF THE CINCHONAS.

§ 1468. The bark of the cinchonas contains two principal alkaloids, to which they owe their medicinal virtue: these are *quinia* and *cinchonin*. Three species of cinchona are known in commerce, the yellow, red, and gray; and while quinin predominates in yellow bark, cinchonin is principally found in the gray; and red bark contains nearly equal proportions of quinin and cinchonin. Two other less important alkaloids are also found in the barks, *chinoidin* and *cinchovatin*, which are present in very small quantities.



§ 1469. Yellow cinchona is preferred for the manufacture of quinin, to which effect the bark is bruised and boiled with water containing 15 or 20 per cent. of sulphuric or chlorohydric acid, when the liquid is filtered through a cloth, and milk of lime added until an alkaline reaction is produced with litmus. The deposit formed, which contains the quinin, is squeezed in a press, and the cake resulting treated with boiling alcohol, three-fourths of which being separated by distillation, sulphuric acid is added to the remainder until a slight persistent acid reaction is obtained. The liquid is discoloured by animal black, and crystallize when the sulphate of quinin crystallizes first, while the sulphate of cinchonin remains in the mother liquid. By decomposing the sulphate of quinin by ammonia, quinin is obtained in the form of a white powder, which, by slow evaporation from an alcoholic solution, is deposited in small prismatic crystals.

Quinin has a very bitter taste, requires for its solution 400 parts of cold and 250 of boiling water, and turns litmus blue. Boiling alcohol dissolves one-half of its weight of it, while ether also dissolves a considerable quantity, and thus furnishes a method of separating it from cinchonin, which is insoluble in ether. The formula of quinin, crystallized from an aqueous solution, is  $C_{38}H_{24}N_2O_4 + 6HO$ , and it loses the 6 equivalents of water at  $248^\circ$ . Quinin, dissolved in alcohol or acidulated water, exerts a rotatory power toward the left, at least at the temperature of  $71.6^\circ$ , the power decreasing as the temperature rises. Quinin forms crystallizable salts with nearly all the acids, its most important compound being the neutral sulphate, used in medicine as an anti-intermittent. Two sulphates of quinin are known.

1. The neutral sulphate, crystallizing in fine silky aciculæ, and very slightly soluble in cold water, of which it requires 750 parts for solution, while it dissolves in 30 parts of boiling water. Its formulæ is  $(C_{38}H_{24}N_2O_4, HO), SO_3 + 7HO$ , and it loses its water of crystallization by heat. It exerts rotation toward the left, like the alkali which acts as its base.

2. The acid sulphate, soluble in 10 or 12 parts of cold water, the formula of which is  $(C_{38}H_{24}N_2O_4, HO)_2SO_3 + 8HO$ , the water of crystallization being driven off by heat.

*Cinchonin*  $C_{38}H_{24}N_2O_2$ .

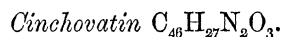
§ 1470. *Cinchonin* is prepared either from the mother liquid of sulphate of quinin, or by treating gray cinchona in the manner by which quinin is extracted from yellow cinchona. Cinchonin crystallizes readily, and without any water of crystallization, its formula being  $C_{38}H_{24}N_2O_2$ , which differs from that of anhydrous quinin only by containing 2 equiv. of oxygen less. Cinchonin is still less soluble in water and alcohol than quinin, while it is insoluble in ether. Salts of cinchonin crystallize readily, and are generally more soluble in water than the corresponding salts of quinin.

When chlorine is made to act upon a concentrated and hot solution of chlorohydrate of cinchonin, a slightly soluble salt is deposited, which, when redissolved in water, and treated with ammonia, forms a precipitate of *bichlorinated cinchonin*  $C_{38}H_{22}Cl_2N_2O_2$ . This substance crystallizes in needles, turns tincture of litmus blue, and forms with acids crystallizable salts, which closely resemble the corresponding salts produced by ordinary cinchonin, and even appear to be isomorphous with them. In the same way bromine converts cinchonin into *bichlorinated cinchonin*  $C_{38}H_{22}Br_2N_2O_2$ . The elementary composition of the bichlorohydrate of bibrominated cinchonin  $C_{38}H_{22}Br_2N_2O_2, 2HCl$  is the same as that of the bibromohydrate of bichlorinated cinchonin  $C_{38}H_{22}Cl_2N_2O_2, 2HBr$ , while the two substances differ essentially from each other, since the former yields with potassa bibrominated cinchonin, and the latter bichlorinated cinchonin.

Cinchonin, dissolved in alcohol or acidulated water, exerts a rotatory power toward the right, while that of quinin is toward the left, and the salts of cinchonin also turns to the right, like the alkali which forms their base, the chlorinated derivatives of the alkali exerting it in the same direction.

*Chinoïdin.*

§ 1471. The mother liquid of sulphate of quinin, after having deposited its sulphate of cinchonin, may yield a small quantity of *sulphate of chinoïdin*. Chinoïdin is as yet but little known, and from the analyses which have been made of it, it would appear to have the same composition as quinin.



§ 1472. *Cinchovatin* is found chiefly in the cinchona from Jaïn, (*cinchona ovata*), from which it is extracted by the same process as quinin. It is a substance insoluble in water, and soluble in alcohol, from which it is deposited in crystals of the formula  $C_{46}H_{27}N_2O_3$ .\*

ALKALOIDS OF OPIUM.

§ 1473. On making incisions into the head of the white poppy, a liquid issues from it, which hardens in the air into a brown horn-like mass, constituting *opium*, the chief part of which is imported from the East, and principally from Smyrna. The poisonous properties of opium are owing to the existence of several alkaloids, the principal of which are *morphin*, *narcotin*, and *codein*; while several others, less important, and only existing in small quantity, are also extracted: *thebain*, *narcein*, *pseudomorphin*, *porphyroxin*, and a non-nitrogenous crystalline substance, which does not act the part of a base, and has been called *meconin*.

First quality opium contains about 10 per cent. of morphin and 5 per cent. of narcotin.



§ 1474. In order to obtain morphin, the opium, cut into thin slices, is macerated for some time with water, and the substance, when softened, is crushed with an additional quantity of water, squeezed in bags under a press, and the cake subjected to similar treatment. The liquid yielded by this process, being evaporated to the consistence of an extract, is again treated with a small quantity of water, which dissolves the salts of morphin, and leaves the greater portion of the narcotin mixed with a brown substance. By testing a small quantity of the liquid, the quantity of ammonia necessary to wholly precipitate this substance is ascertained, while only  $\frac{1}{3}$  of this quantity is poured into the whole liquid, when the impure morphin is precipitated, carrying with it nearly all the colouring matter. By

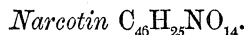
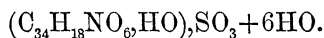
\* *Arizin* is not mentioned by Regnault, and in fact much uncertainty exists as to the alkaloids in cinchona bark, except quinine and cinchona.—J. C. B.

then adding the balance of the ammonia, nearly pure morphin is precipitated, and is treated with alcohol marking 20° of Baumé, which does not sensibly dissolve the morphin, while it removes almost entirely the resinous matter which adulterates it. The residue is then treated with boiling alcohol at 35° Baumé, which dissolves the morphin and deposits the greater part of it on cooling. Three-fourths of the alcohol are deposited by distillation and the residue yields the balance of the morphin.

In order to obtain the base perfectly pure, it is best to redissolve it in weak chlorohydric acid, crystallize the chlorohydrate, and again decompose this salt by ammonia.

Morphin readily forms crystals of the formula  $C_{34}H_{18}NO_6 + 2HO$ , which lose the 2 equiv. of water by an elevation of temperature, and may be heated to 570° without injury. Cold water dissolves about  $\frac{1}{1000}$  of morphin, and hot water nearly double of that quantity; the solution showing an alkaline reaction with litmus. Weak alcohol at 20° B. dissolves but very little morphin, while boiling alcohol at 35° B. dissolves  $\frac{1}{25}$  of its weight, the greater portion of the morphin crystallizing on cooling. It is scarcely soluble in ether, but a concentrated solution of caustic potassa dissolves it without change, by which process the base may be separated from narcotin, the latter being insoluble in alkaline lixivie. Morphin dissolved in acidulated water exerts a rotatory power toward the left, like its salts.

Morphin forms crystallizable salts with acids, soluble in water and alcohol, but insoluble in ether. Chlorohydrate of morphin, which is most important on account of its use in medicine, crystallizes in silky tufts, and dissolves in 1 part of boiling or in 20 parts of cold water. Its formula is  $C_{34}H_{18}NO_6 \cdot HCl + 6HO$ , while that of crystallized sulphate of morphin is



§ 1475. Narcotin is extracted from the residues left after the extraction of morphin from opium by treating them with ether, which dissolves a mixture of narcotin and porphyroxin, the narcotin greatly predominating. Fresh opium may also be treated directly with ether, when the salts of morphin remain in the residue and the ether contains, with the narcotin and porphyroxin, a certain quantity of meconin. The ether being distilled in a water-bath and the residue treated with water, which dissolves the meconin, the narcotin and porphyroxin are finally dissolved in dilute chlorohydric acid. The solution, when evaporated, deposits chlorohydrate of narcotin, while the chlorohydrate of porphyroxin remains in the mother liquid. The chlorohydrate of narcotin, decomposed by ammonia, yields isolated narcotin, which is purified by crystallizing it in alcohol.

Narcotin crystallizes in small rhomboidal prisms, melting at  $338^{\circ}$ , decomposing at about  $390^{\circ}$ , insoluble in cold water, and only dissolving in 500 parts of boiling water. Alcohol, when hot, dissolves about  $\frac{1}{30}$  of its weight, and ether  $\frac{1}{60}$ . Narcotin is a much more feeble base than the alkaloids we have hitherto described, since its solutions do not turn to blue the reddened tincture of litmus, although it forms crystallizable salts with acids. The formula of narcotin is  $C_{46}H_{25}NO_{14}$ , while that of the chlorohydrate is  $C_{46}H_{25}NO_{14},HCl$ . Narcotin, dissolved in alcohol or acidulated water, exerts a rotatory power to the right, opposite to that of morphin; the salts of narcotin possessing the same power as the alkali.

*Codeïn*  $C_{34}H_{19}NO_5$ .

§ 1476. Codeïn remains in the liquid from which morphin has been precipitated by ammonia, and is extracted by concentrating them through evaporation, adding caustic potassa, and then continuing the evaporation to dryness. The residue is treated with ether, which dissolves the codeïn, and yields, by spontaneous evaporation, large crystals of this substance, which are remarkable for the sharpness of their configuration.

Codeïn, which is much more soluble than the other alkaloids of opium, since it dissolves in 80 parts of cold and 20 of boiling water, turns the reddened tincture of litmus blue, and is also highly soluble in alcohol and ether. The formula of codeïn, crystallized in water, is  $C_{34}H_{19}NO_5 + 2HO$ , and heat readily drives off its 2 equiv. of water, while it crystallizes in the anhydrous state from its solutions in ether.

Codeïn has been used for some time in medicine.

ALKALOIDS OF STRYCHNOS.

*Strychnin*  $C_{42}H_{22}N_2O_4$  and *Brucin*  $C_{46}H_{26}N_2O_8$ .

§ 1477. The majority of the genus of *strychnos*, particularly the bean of St. Ignatius, (*strychnos Ignatia*), nux vomica, (*strychnos nux vomica*), viper-wood, (*strychnos colubrina*), and the upas tieuté, (*strychnos tieuté*), contain two alkaloids in various proportions, *strychnin* and *brucin*, remarkable for the very poisonous effect they exert on the animal economy.

The two bases are generally extracted from nux vomica by boiling the powdered nut with water containing its weight of sulphuric acid, expressing the liquid, and precipitating the two bases by hydrated lime. The deposit is treated with boiling alcohol, which dissolves the strychnin and brucin; and, on cooling, the greater portion of the strychnin crystallizes. The liquid, concentrated by evaporation, yields less pure strychnin, and the brucin crystallizes last. It is necessary to purify these substances by several successive crystallizations.

Strychnin crystallizes readily in octohedrons with rectangular bases, insoluble in water, slightly soluble in alcohol, and presenting the formula  $C_{42}H_{22}N_2O_4$ . It forms easily crystallizable salts, and the formula of crystallized chlorohydrate of strychnin is  $C_{42}H_{22}N_2O_4 \cdot HCl + 3HO$ , while that of the crystallized sulphate is  $(C_{42}H_{22}N_2O_4 \cdot HO)_2SO_3$ . Strychnin, dissolved in acidulated water, exerts a rotatory power toward the left, like its salts.\*

Brucin crystallizes in right prisms with a rhombic base, and its formula is  $C_{46}H_{26}N_2O_8 + 8HO$ ; the 8 equiv. of water being given off by heat. Water dissolves a small quantity of it, and it is much more soluble in alcohol than strychnin. Concentrated nitric acid produces an intense red colour with brucin, which property distinguishes it from a majority of the other alkaloids. Brucin dissolved in alcohol, or in water to which no acid has been added, deviates to the left like strychnin, its salts presenting the same behaviour.

#### ALKALOID OF COFFEE AND TEA.

##### *Caffeïn or Theïn* $C_8H_5N_2O_2$ .

§ 1478. Coffee and tea contain the same alkaloid, which is called *caffëin* or *theïn*, according as it has been extracted from either of these substances, because it was at first supposed that they were not identical. In order to extract *caffëin* from coffee, the bruised coffee-grains are treated with water, and subacetate of lead is poured into the liquid, after which, the deposit being separated, sulphydric acid is passed through in order to precipitate the excess of lead. The solution being then evaporated, the *caffëin* crystallizes, and is purified by successive crystallizations. *Theïn* is extracted in precisely the same manner.

*Caffeïn* crystallizes in silky aciculæ, taking the formula  $C_8H_5N_2O_2 + 2HO$ , while it loses its 2 equivalents of water at  $212^\circ$ , melts at about  $356^\circ$ , and sublimes above  $570^\circ$ . It is soluble in water, alcohol, and ether; and its basic affinities are very feeble, for although it dissolves in acids, it generally leaves them when the solution is evaporated.

#### VOLATILE NATIVE ALKALOIDS.

§ 1479. Two native alkaloids are now known, which volatilize without change: *nicotin*, or the alkali of tobacco, and *conicin*, the alkali of cicuta.

##### *Nicotin* $C_{20}H_{14}N_2$ .

§ 1480. Certain varieties of tobacco contain 7 or 8 per cent. of *nicotin*, which is extracted by digesting the tobacco-leaves with

\* The elementary composition of this most violent poison is, singular enough, identical with that of rye bread, a most wholesome article of food. The natives of Borneo use the juice of the different kinds of *strychnos* for poisoning their arrow-heads, the wound of which is generally fatal.—*W. L. F.*

water, evaporating the infusion to the consistence of an extract, and then treating with alcohol, which is, in its turn, concentrated, after being decanted. The new extract is treated with potassa, and then shaken with ether, which dissolves the nicotin as well as some foreign substances. Finely powdered oxalic acid is added to the ethereal solution, which is to be frequently shaken, when oxalate of nicotin is formed, and precipitated in drops, which are washed several times with water. The oxalate of nicotin being decomposed by potassa, free nicotin is separated by ether. The ethereal solution is distilled in a retort over a water-bath, when the greater portion of the ether distils rapidly, while the last particles do not pass over at  $212^{\circ}$ ; and there exists also a small quantity of ammonia and water, which separate only at a higher temperature. The retort must be kept, for a whole day, at a temperature of  $284^{\circ}$ , and a feeble current of hydrogen must be passed through it, after which the receiver is changed, and the temperature raised to  $356^{\circ}$ , in order to distil the nicotin in a current of hydrogen.

Nicotin is an oleaginous, limpid, and colourless liquid, smelling slightly of tobacco, and which boils at  $473^{\circ}$ , but begins to decompose at this temperature; so that it is necessary to distil it under feeble pressure, or in a current of hydrogen gas, so as not to be obliged to raise the temperature to a degree at which the elastic force of the vapour is equal to the pressure of the atmosphere. The density of liquid nicotin is 1.048, while the density of its vapour has been found to be 5.607. Nicotin is very soluble in water, which then reacts powerfully alkaline; and caustic potassa precipitates it from its solutions in the form of oleaginous drops, while ether takes it from water and dissolves it in all proportions, alcohol also dissolving a large quantity of it. It is one of the most powerful poisons. Nicotin soon changes in the air, by absorbing oxygen, and is converted into a brown substance of a resinous appearance.

The salts of nicotin are in general very soluble, and crystallize with difficulty. The formulæ of the sulphate and nitrate of nicotin are  $(C_{20}H_{14}N_2, HO), SO_3$  and  $(C_{20}H_{14}N_2, HO), NO_5$ , according to which the formula of free nicotin is  $C_{20}H_{14}N_2$ , corresponding to 4 volumes of vapour, like that of ammonia. Nicotin exerts an extremely energetic rotatory power toward the left, while its chlorohydrate turns the plane of polarization with the same power toward the right.

The various species of tobacco contain very different proportions of nicotin, the following quantities having been found in 100 parts of dry tobacco:

Foreign Tobacco.	French Tobacco.
Havana..... 2.0	Alsace..... 3.2
Maryland ..... 2.3	Pas-de-Calais..... 4.9
Virginia..... 6.9	Nord..... 6.6
	Lot..... 8.0

The tobacco which contains most nicotin is the best for the manu-



facture of snuff, since the property possessed by tobacco of stimulating the mucous membrane of the nose, is owing to the presence of nicotin and ammoniacal salts.

*Conicin*  $C_{16}H_{15}N$

§ 1481. Conicin is extracted from the seeds of the conium, but it is also found in the leaves and stalk of this plant, previous to its flowering. The bruised seeds being distilled with a solution of potassa, conicin passes over with water and ammonia. The liquid is saturated with sulphuric acid, and evaporated to the consistence of syrup; when, by treating the extract with a mixture of alcohol and ether, the sulphate of conicin is dissolved, while the ammoniacal sulphate is left. The solution of the sulphate of conicin is then evaporated, and afterward decomposed by caustic potassa; when the conicin arising from this decomposition is decanted, and then left for some time on chloride of calcium, which abstracts its water, after which it is purified by distillation.

Conicin is a colourless liquid, having a sharp smell, which immediately produces sickness, and its density is 0.89, while it boils at  $338^{\circ}$ . It is one of the most powerful poisons. Conicin is slightly soluble in water, but dissolves in all proportions in alcohol and ether, its solutions showing a strong alkaline reaction. It rapidly absorbs the oxygen of the air, and then assumes various shades of colour. The salts of conicin are in general deliquescent and not crystalline; and the composition of the alkaloid corresponds to the formula  $C_{16}H_{15}N$ .

ARTIFICIAL ALKALOIDS.

§ 1482. Chemists have long since succeeded in preparing a great number of alkaloids, which have not yet been found in vegetables. Almost all these alkaloids are volatile without decomposition, and contain no oxygen; and while some resemble, in their properties, nicotin and conicin, others are so closely analogous to ammonia, that, in a purely philosophical classification of substances, it would be impossible to separate them from that base.

*Quinoleïn*  $C_{18}H_7N$ .

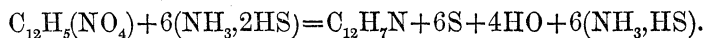
§ 1483. Several native organic bases, particularly quinin, cinchonin, and strychnin, yield, by distillation with potassa, a volatile alkaloid called *quinoleïn*. It is obtained in greatest quantity from cinchonin, by heating in a tubulated retort some fragments of caustic potassa with a small quantity of water, so as to form a pasty solution, and gradually adding powdered cinchonin. It is heated with an alcohol-lamp until the substance appears to be dried, when hydrogen is disengaged, while water passes over, as also an oily substance, which is rectified a second time over potassa. Quinoleïn is a colourless oil, of a disagreeable odour, distilling at about  $446^{\circ}$ ,

insoluble in cold, and scarcely soluble in boiling water, while alcohol and ether dissolve it freely. It forms crystallizable salts with chlorhydric, sulphuric, and nitric acids, and it contains no oxygen, its formula being  $C_{12}H_7N$ . Quinolein is also found among the products of distillation of coal-tar, and was formerly called *leucole*.

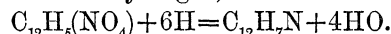
#### ALKALOIDS DERIVED FROM VARIOUS CARBURETTED HYDROGENS.

##### *Anilin* $C_{12}H_7N$ .

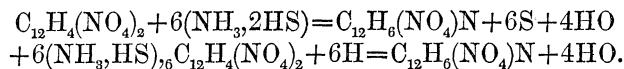
§ 1484. The majority of the carburetted hydrogens yield, when they are boiled with monohydrated nitric acid, or a mixture of this acid and concentrated sulphuric acid, nitrogenous substances, which result from the substitution of 1 equivalent or 2 equivalents of the compound  $NO_4$  in the place of 1 or 2 equivalents of hydrogen. Thus, we shall soon see that benzin  $C_{12}H_6$ , treated with monohydrated nitric acid, produces two substances, *nitrobenzin*  $C_{12}H_5(NO_4)$  and *binitrobenzin*  $C_{12}H_4(NO_4)_2$ . These nitrogenous compounds yield alkaloids when they are subjected to the action of reducing substances, as *e. g.* the sulphydrate of ammonia, or to the action of nascent hydrogen obtained by causing dilute sulphuric acid to act on zinc in contact with the nitrogenous substance. Thus, by the action of the bisulphydrate of ammonia on nitrobenzin, we obtain an alkaloid, *anilin*  $C_{12}H_7N$ , from the following reaction:



By the action of nascent hydrogen, we have



When binitrobenzin is subjected to the same treatment, there results a second alkaloid, *nitranilin*  $C_{12}H_6(NO_4)N$ , according to the following reactions:



We shall describe only anilin and nitranilin; the properties of the numerous alkaloids obtained by applying the same processes to other carburetted hydrogens, or substances derived from them, being very similar.

Anilin is a colourless liquid, of an agreeable vinous smell, boiling at  $359.6^\circ$ , and dissolving slightly in water, but in all proportions in alcohol and ether. Anilin possesses no rotatory power. Chlorine and bromine convert it into chlorinated or brominated substances, modified merely by substitution, and which often retain the basic properties and capacity of saturation of the original anilin. Monochlorinated anilin  $C_{12}H_6ClN$ , the monobrominated  $C_{12}H_6BrN$ , and nitranilin  $C_{12}H_6(NO_4)N$ , are bases which form salts as well defined as anilin itself; while the terchlorinated  $C_{12}H_4Cl_3N$  and terbrominated anilins  $C_{12}H_4Br_3N$  possess no basic properties.

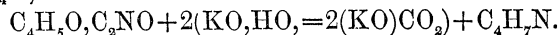
Iodine may also be substituted for hydrogen in anilin, and a *moniodinated anilin*  $C_{12}H_6IN$  has been obtained which combines with acids. Cyanogen gives rise to no phenomena of substitution, but combines directly with anilin with the evolution of heat, and produces a new crystallizable base, *cyanilin*  $C_{12}H_7NCy=C_{14}H_7N_2$ , which forms, with the majority of acids, well-defined and crystallizable salts.

ALKALOIDS DERIVED FROM CYANIC AND CYANURIC ETHERS,  
PRESENTING A CLOSE ANALOGY WITH AMMONIA.

§ 1485. We shall subsequently describe, together with some other products of cyanogen, two isomeric compounds of this substance with oxygen, *cyanic acid*  $CyO=C_2NO$ , and *cyanuric acid*  $Cy_3O_3=C_6N_3O_3$ , which are readily converted into each other, as will be shown in its place. These acids combine with bases, forming cyanates and cyanurates.

*Ethylammonia*  $C_4H_5(NH_2)$ .

§ 1486. By distilling cyanate of potassa  $KO, CyO$  with a solution of sulphovinate of potassa  $KO, (C_4H_5O, 2SO_3)$  there is obtained a mixture of *cyanic ether*  $C_4H_5O, CyO$  and *cyanuric ether*  $3C_4H_5O, Cy_3O_3$ , which are easily separated by distillation, the first being very volatile, while the second boils only at a very high temperature. Cyanic ether dissolves in ammonia with disengagement of heat, and the liquid, when evaporated, deposits beautiful prismatic crystals, which are fusible, very soluble in water and alcohol, and of the formula  $C_6H_8N_2O_2$ : they result therefrom from the simple combination of 1 equivalent of cyanic ether  $C_4H_5O, CyO=C_6H_5NO_2$  with 1 equivalent of ammonia  $NH_3$ . Cyanic and cyanuric ethers, treated with caustic potassa, yield carbonate of potassa and an alkaloid  $C_4H_7N$ :



We shall call this alkaloid *ethylammonia*, and its formula  $C_4H_7N$  may be written  $C_4H_4NH_3$ , considering it as resulting from the combination of 1 equivalent of ammonia with 1 equivalent of bicarburetted hydrogen  $C_4H_4$ , while it may also be written  $C_4H_5(NH_2)$ , and the alkaloid regarded as belonging to the series of simple ethers. One of the equivalents of hydrogen and carburetted hydrogen  $C_4H_6$ , the generator of the series, having been replaced by 1 equivalent of amide  $(NH_2)$ .

In order to obtain ethylammonia, cyanic or cyanuric ether is boiled in a distilling apparatus with an excess of potassa, the vapours being collected in a well-cooled receiver containing a small quantity of water, which takes the ethylammonia in solution, and thus becomes strongly alkaline, with an intense ammoniacal odour, although it does contain a trace of free ammonia. This liquid is saturated with chlorohydric acid and evaporated, when crystals are

obtained which dissolve completely in absolute alcohol, and are again deposited, by evaporation, in crystalline lamellæ. This compound is chlorohydrate of ethylammonia  $C_2H_5N, HCl$ , and is distinguished from chlorohydrate of ammonia by its solubility in absolute alcohol.

The chlorohydrate of ethylammonia, perfectly dried, is mixed with double its weight of quicklime, and introduced into a long tube closed at one end, so as to fill one-half of it; and the other half being filled with fragments of caustic potassa, a disengagement-tube, which enters a flask surrounded by a refrigerating mixture, is adapted to it. Gentle heat being applied, the ethylammonia set free distils, and is condensed in the receiver. It is important to remark that this process exactly resembles that used for obtaining ammonia.

Ethylammonia is a colourless, very volatile liquid, boiling at  $64.4^\circ$ , exhaling a very penetrating ammoniacal odour, turning blue the reddened tincture of litmus, and exhibiting a causticity resembling that of potassa. When a glass rod moistened with chlorohydric acid is brought near it, extremely thick white fumes are produced; and each drop of acid poured into it produces a hissing at the moment of its mixing with the base. Ethylammonia ignites when brought near to a substance in combustion, and burns with a bluish flame. It mixes with water in all proportions, becoming very hot, and giving rise to a solution of which the basic properties absolutely resemble those of ammonia. A solution of ethylammonia precipitates, in fact, the salts of magnesia, alumina, manganese, iron, bismuth, chrome, uranium, tin, lead, and mercury. Salts of zinc throw down a white precipitate, which redissolves in a large excess of the reagent. Salts of copper produce a bluish white precipitate, readily soluble in an excess of the reagent, furnishing a deep-blue liquid, analogous to that produced by an excess of ammonia, (§ 1046.)

Ethylammonia combines with all the acids, forming crystallizable salts precisely resembling those of ammonia, and it also furnishes compounds analogous to the amides, (§ 514.) In fact, by mixing a solution of ethylammonia with oxalic ether, the mixture becomes cloudy, and alcohol is formed, while acicular crystals of a compound  $C_6H_6NO_2 = C_4H_6N, C_2O_2$  corresponding to oxamide  $NH_2, C_2O_2$  separate.

*Methylammonia*  $C_2H_5N$  or  $C_2H_3(NH_2)$ .

§ 1487. By boiling methylocyanic or methylocyanuric ether with a solution of potassa, and collecting the product in a well-cooled receiver containing water, a strongly alkaline solution is obtained, which exhales a very penetrating ammoniacal odour. It is saturated with chlorohydric acid, evaporated to dryness, and again treated with boiling alcohol, which deposits, on cooling, pearl-like

crystalline lamellæ of *chlorohydrate of methylammonia*  $C_2H_5N, HCl$ . This salt heated with quicklime, as in the preparation of ammonia and ethylammonia, yields *methylammonia*, which may be obtained in the form of a colourless liquid by cooling the receiver with a proper refrigerating mixture. Methylammonia is gaseous at the ordinary temperature, and may be collected in bell-glasses over mercury, when it resembles ammoniacal gas so closely as to require peculiar attention to distinguish it from it.

Methylammonia liquefies at about  $32^\circ$ , and its odour is strongly ammoniacal, while its density is 1.08, its chemical equivalent  $C_2HN_5$ , corresponding, like that of ammonia, to 4 volumes of gas. Methylammoniacal gas is the most soluble of all gases known, since, at  $53.6^\circ$ , 1 volume of water dissolves 1040 volumes of it, while at  $77^\circ$  water only takes up 906. Like ammoniacal gas, it is instantaneously absorbed by charcoal, but it is distinguished from the latter gas by igniting by contact with a lighted candle and burning with a yellowish flame. It produces, with metallic solutions, reactions precisely similar to those of ammonia or ethylammonia.

*Amylammonia*  $C_{10}H_{13}N$  or  $C_{10}H_{11}(NH_2)$ .

§ 1488. The oil of potato-spirit  $C_{10}H_{12}O_3$  exhibits, as shall soon be shown, a perfect analogy with vinic and methylic alcohols, in the products which it forms with chemical agents, for which reason it has been called *amylic alcohol*. If amylocyanic or amylocyanuric ether be distilled with a solution of potassa, carbonate of potassa is obtained, besides a new base, *amylammonia*  $C_{10}H_{13}N$ , which formula may be written  $C_{10}H_{10}NH_3$ , because carburetted hydrogen  $C_{10}H_{10}$  is, in the amylic series, the analogue of bicarburetted hydrogen in the vinic series. It may be also written  $C_{10}H_{11}(NH_2)$ , if it be considered as resulting from the replacing of 1 equivalent of hydrogen, in the amylic molecule  $C_{10}H_{12}$ , by 1 equivalent of amide ( $NH_2$ ). Amyl is found in solution in the water which has passed over in distillation; by saturating which with chlorohydric acid, white crystalline lamellæ, soluble in water and alcohol, of *chlorohydrate of amyllummonia*  $C_{10}H_{13}N, HCl$ , are obtained after evaporation. This salt, distilled with quicklime, yields amyllummonia in the form of a colourless liquid, of a strong ammoniacal odour, and very soluble in water.

Amyllummonia precipitates all the metallic salts which are precipitated by ammonia; and with solutions of copper, it yields a precipitate which dissolves in an excess of the reagent and colours the liquid blue: nevertheless, to effect perfect solution, a larger proportion of amyllummonia must be used than of ethylammonia or methylammonia. Chloride of silver also dissolves in it, but less readily than in ammonia.

Amyllummonia forms with acids a great number of crystallizable acids.

*Butyrylammonia*  $C_8H_{11}N$  or  $C_8H_9(NH_2)$ .

§ 1489. Butyrylammonia has not yet been prepared by the general process which has furnished the foregoing volatile alkaloids; while among the products of distillation of animal substances, several volatile alkaloids have been found, among which one called *petinin*  $C_8H_{11}N$  is distinguished, presenting exactly the composition of butyrylammonia. The composition of this substance presents, in fact, with that of butyric acid  $C_8H_7O_3.HO$ , the relation which exists between ethylammonia  $C_4H_7N$  and acetic acid  $C_4H_3O_3.HO$ . It is a colourless liquid, of a penetrating ammoniacal odour, and forming well-defined salts with acids.

§ 1490. The resemblance with ammonia of the last volatile alkaloids which we have described, is as perfect as that observed between potassa and soda; and their composition presents the remarkable peculiarity, that they may be considered as formed by the union of 1 equivalent of ammonia with a carburetted hydrogen. The other volatile alkalies, either native or artificial, which we have described, exhibit a similar grouping in their composition, and should probably be included in a single class, which will, certainly, be subsequently greatly extended. Thus we have,

Ammonia*	.....	$NH_3$
Methylammonia	.....	$NH_3, C_2H_2,$
Ethylammonia	.....	$NH_3, C_4H_4,$
Butyrylammonia	.....	$NH_3, C_8H_8,$
Amylammonia	.....	$NH_3, C_{10}H_{10},$
Nicotin	.....	$NH_3, C_{10}H_4,$
Anilin	.....	$NH_3, C_{12}H_4,$
Conicin	.....	$NH_3, C_{16}H_{12},$
Quinoleïn	.....	$NH_3, C_{18}H_4.$

## OF SOME NEUTRAL SUBSTANCES FOUND IN VEGETABLES.

§ 1491. In the following chapter we shall describe certain substances found in vegetables, exhibiting no well-marked characters of acidity or alkalinity, and which have hitherto not been attached

\* The first five compounds in the above table may be considered as ammonia paired with respectively 0, 1, 2, 4, and 5 equivalents of the carburetted hydrogen  $C_2H_2$ , or olefiant gas; which, according to the theory of pairing, explained in the note to § 1401, would fully explain the ammoniacal properties of the paired compounds. They may also be regarded, with equal propriety, as ammonias in which 1 equivalent of hydrogen is replaced by 1 equivalent of the radicals methyl, ethyl, butyryl, and amyl, respectively; which view has gained much probability by the recent investigations of Frankland and Kolbe.—*W. L. F.*

to any of the great series of organic compounds. These substances being very numerous, we shall only mention the most important and those which are best known.

*Piperin*  $C_{34}H_{18}NO_6$ .

§ 1492. Piperin exists in pepper, and is generally extracted from white pepper, by treating it with alcohol. The alcoholic solution is evaporated, the residue treated with an alkaline lye, which dissolves various substances, and leaves the piperin isolated. It is to be purified by several crystallizations in alcohol. Piperin forms colourless prisms, which melt at about  $212^\circ$ , and is slightly soluble in water, but very soluble in alcohol. Acids dissolve it readily, without forming a fixed compound with it, and, if they are volatile, they part with it wholly by evaporation, which operation is even effected at the ordinary temperature in vacuo. The composition of piperin corresponds to the formula  $C_{34}H_{18}NO_6$ , showing it to be isomeric with morphin.

*Picrotoxin*  $C_{12}H_7O_5$ .

§ 1493. Picrotoxin is the poisonous principle of the *cocculus Indicus*, and is obtained by exhausting these berries by alcohol, and evaporating the liquor, when a mixture of picrotoxin with fatty matter remains as a residue. The residue is pressed between folds of tissue-paper, and then redissolved in alcohol, after which the liquor is bleached by animal black, and picrotoxin obtained, by evaporation, in small acicular crystals. Picrotoxin dissolves in 25 parts of boiling water, the greater portion of it being again deposited on cooling, while it dissolves readily in alcohol. Picrotoxin does not combine with acids, and it contains no nitrogen, its composition corresponding to the formula  $C_{12}H_7O_5$ .

*Cantharidin*  $C_{10}H_6O_4$ .

§ 1494. Cantharidin, the active principle of cantharides, possesses extremely powerful vesicating properties, and if any portion of the body be exposed to its vapours, swelling accompanied by acute pain immediately ensues. It is obtained by treating powdered cantharides with alcohol, and evaporating the alcohol, when an aqueous liquid remains, on which floats an oily coat, solidifying on cooling. This coat being dissolved in alcohol and discoloured by animal black, crystals of cantharidin are obtained by evaporation. Cantharidin contains no nitrogen, and its composition corresponds to the formula  $C_{10}H_6O_4$ ; but its equivalent has not yet been determined, as no definite compound of it is known. Cantharidin is insoluble in water, but dissolves readily in alcohol and ether.

*Asparagin*  $C_8H_7N_2O_5, HO$ .

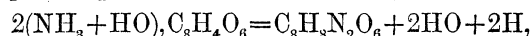
§ 1495. The name of *asparagin* has been given to a crystallizable substance, first found in the shoots of asparagus, but which also

exists in liquorice-root, in marsh-mallow root, comfrey, potatoes, vetches, and several other plants. It is generally prepared by macerating bruised marsh-mallow roots with very clear milk of lime, filtering the liquid, precipitating the dissolved lime by carbonate of ammonia, and evaporating to the consistence of syrup; when, in the course of a few days, granular crystals of impure asparagin separate, which are purified by recrystallization.

Asparagin does not originally exist in the seeds of the vetch, but is developed during germination and vegetation, to again disappear at the flowering period. In order to extract it, the plant is cut at the proper season, and the juice expressed and boiled, when albuminous substances coagulate and are separated. The liquid being evaporated to the consistence of syrup, and left to itself, deposits crystals of asparagin, which are purified by being washed with cold water and recrystallized several times.

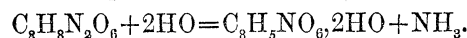
Asparagin forms beautiful colourless prismatic crystals, requiring for solution about 60 parts of water, at the ordinary temperature, but dissolving more freely in boiling water. It is not sensibly soluble in absolute alcohol or in ether. Its aqueous solution feebly reddens litmus; and when it is poured into a hot solution of acetate of copper, a beautifully blue precipitate is formed, consisting of a compound with oxide of copper, of the formula  $\text{CuO}, \text{C}_8\text{H}_7\text{N}_2\text{O}_6$ . The formula of asparagin dried at  $212^\circ$  is  $\text{C}_8\text{H}_6\text{N}_2\text{O}_6$ , which should be written  $\text{C}_8\text{H}_7\text{N}_2\text{O}_6, \text{HO}$ ; while the formula of crystallized asparagin is  $\text{C}_8\text{H}_7\text{N}_2\text{O}_6, \text{HO} + 2\text{HO}$ .

A solution of pure asparagin, left to itself, remains unchanged for an indefinite length of time, which is not the case if it contains some of the principles which accompany it in the vegetable, when it undergoes a kind of fermentation which converts it into succinate of ammonia. If we observe that 1 equivalent of succinate of ammonia is equal, in its elementary composition, to 1 equivalent of asparagin plus 2 equivalents of water and 2 equivalents of hydrogen,



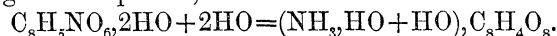
we may admit that asparagin assimilates to itself 2 equivalents of water and 2 equivalents of hydrogen, produced by the putrefaction ensuing in the liquid, which excites a reducing action in nearly all analogous cases.

Under the influence of sulphuric and chlorohydric acid, and of nitric free from nitrous acid, asparagin is decomposed into ammonia and a new acid, called *aspartic*  $\text{C}_8\text{H}_5\text{NO}_6, 2\text{HO}$ , which is very slightly soluble in water, but readily so in the acids, with which it afterward parts with difficulty by evaporation. It crystallizes in small pearly leaflets; and may also be obtained by boiling asparagin with a solution of potassa, when ammonia is disengaged, and the liquor contains aspartate of potassa,





If asparagin be treated with nitric acid containing nitrous acid, a considerable quantity of bimalate of ammonia ( $\text{NH}_3, \text{HO} + \text{HO}$ ),  $\text{C}_8\text{H}_4\text{O}_8$  is formed, nitrogen being disengaged at the same time. Under the influence of the nitric acid, the asparagin is converted into aspartic acid and ammonia, while the ammonia has been consumed by the nitrous acid, yielding water and free nitrogen; and the aspartic acid, having combined with 2 equivalents of water in the nascent state, has been changed into bimalate of ammonia, according to the equation,



It is proper to observe that aspartic acid and asparagin may be considered as malic acid, united to 1 or 2 equivalents of ammonia  $\text{NH}_3$ ; that is, as two amides of malic acid. This view of the constitution of these substances is corroborated by the fact that the other amides, such as oxamide, butyramide, etc., yield, with nitric charged with nitrous acid, decompositions analogous to those produced by aspartic acid and asparagin, and are converted into oxalic, butyric acid, etc., with disengagement of nitrogen.

*Phloridzin*  $\text{C}_{24}\text{H}_{18}\text{O}_4$ .

§ 1496. Phloridzin exists in the fresh bark of the apple, pear, plum, and cherry tree, and is generally extracted from the bark of the roots of the apple, by digesting it in weak alcohol, when the phloridzin dissolves and separates by evaporation in silky aciculæ, which are purified by recrystallization in alcohol. Boiling water dissolves a large quantity of phloridzin, while it scarcely retains  $\frac{1}{1000}$  part of it after cooling; and alcohol dissolves it readily, the solution exerting no reaction on litmus. The solution of phloridzin in alcohol exerts a rotatory power toward the left. It loses water when heated, and is subsequently decomposed at about  $392^\circ$ . Dilute mineral acids dissolve phloridzin when cold, while if heat be applied the liquid becomes clouded, and deposits a new substance, *phloretin*  $\text{C}_{12}\text{H}_7\text{O}_5$ , which is obtained in crystalline lamellæ by solution in alcohol.

*Glycyrrhizin*  $\text{C}_{36}\text{H}_{22}\text{O}_{12}, 2\text{HO}$ .

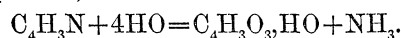
§ 1497. This name has been given to a sweet substance found in the aqueous extract of liquorice-root, (*glycyrrhiza glabra*), from which it is extracted by adding to the concentrated liquid almost any acid, which yields a flaky precipitate collecting into a tarry mass. This substance, when dried, is dissolved in absolute alcohol, which again deposits it, by evaporation, in the form of an amorphous brownish-yellow mass. Glycyrrhizin is but slightly soluble in cold water, and nearly insoluble when the water contains an acid; while it dissolves freely in absolute alcohol, but is insoluble in ether. Analysis has assigned to it the formula  $\text{C}_{36}\text{H}_{22}\text{O}_{12}, 2\text{HO}$ , and its solution produces, with acetate of lead, a precipitate of the formula  $2\text{PbO}, \text{C}_{36}\text{H}_{22}\text{O}_{12}$ .

## NITRILS.

§ 1498. By causing anhydrous phosphoric acid to act on the ammoniacal salts formed by the organic acids, or on the corresponding amides, a new class of substances, called *nitrils*, is obtained, the composition of which may be represented by cyanhydrates of carburetted hydrogen, and which regenerate, by the action of the alkalies, the acid of the original ammoniacal salt, by seizing on the water and disengaging ammonia. We shall give some examples of their curious reactions.

*Acetonitril*  $C_4H_3N$ .

§ 1499. By heating crystallized acetate of ammonia with anhydrous phosphoric acid, a liquid is obtained soluble in water in all proportions. In order to purify it, it is first digested over chloride of calcium, and then distilled successively over chloride of calcium and calcined magnesia. The liquid, which is called *acetonitril*,\* boils at  $170.6^\circ$ , and its formula  $C_4H_3N$  corresponds to 4 vol. of vapour. In contact with hydrated potassa, ammonia and acetic acid are regenerated:



Potassium decomposes it when cold, cyanide of potassium being formed, and a mixture of hydrogen and carburetted hydrogen disengaged.

Acetonitril appears to be identical with methylocyanohydric ether  $C_2H_3, C_2N$ , but alkalies do not act upon it as upon other compound ethers, since they convert it into acetic acid and ammonia.

Acetonitril is also produced when *acetamide*  $C_4H_3O_2, NH_2$  is heated with anhydrous phosphoric acid. Acetamide, which is obtained by treating acetic ether with ammonia, is white, and crystallizes in prismatic aciculæ, melting at  $172.4^\circ$ , and boiling at about  $428^\circ$ .

Chloracetate of ammonia  $(NH_3, HO), C_4Cl_3O_3$  and chloracetamide  $C_4Cl_3O_2, NH_2$  furnish, with anhydrous phosphoric acid, *perchlorinated acetonitril*  $C_4Cl_3N$ , which boils at  $177.8^\circ$ , and yields chloracetic acid, when the corresponding compound forms acetic acid.

*Butyronitril*  $C_8H_7N$ .

§ 1500. The butyrate of ammonia and butyramide, heated with anhydrous phosphoric acid, yield butyronitril  $C_8H_7N$ , an oily liquid, boiling at  $245.3^\circ$ , and which potassium converts into cyanide of potassium, hydrogen, and a new carburetted hydrogen. Its formula  $C_8H_7N$  corresponds to 4 vol. of vapour.

*Valeronitril*,  $C_{10}H_9N$ .

§ 1501. Valeramide, heated with anhydrous phosphoric acid, produces valeronitril  $C_{10}H_9N$ , a colourless liquid, boiling at  $257^\circ$ , which is decomposed by potassium, when cold, into cyanide, hydrogen, and a new carburetted hydrogen.

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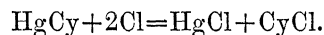
\* It may be termed methylocyanohydric acid.—*J.C.B.*

## PRODUCTS OF CYANOGEN.

§ 1502. Cyanogen is always a product of the decomposition by heat, in the presence of alkalies, of nitrogenous organic substances. Its study, and that of its numerous derivatives, should therefore find a place among substances of the organic kingdom; but its compounds play too considerable a part in chemical processes and are too frequently used in the examination of the salts of various metals to allow us to postpone their consideration until the end of the course. These reasons have induced us to describe, in the first part of our course, cyanogen and its compound with hydrogen, cyanohydric acid. We have seen that cyanogen behaves, in its compounds, like the simple metalloid substances, particularly like chlorine, and we have described in detail the principal compounds it forms with the metals, the simple and multiple cyanides, which are very important compounds, both on account of their use in dyeing, and in chemical analysis. It still remains to us to describe the compounds of cyanogen with several metalloids, chlorine, iodine, oxygen, sulphur, and several more complicated combinations, which present some points of peculiar interest for our chemical theories.

## COMPOUNDS OF CYANOGEN WITH CHLORINE.

§ 1503. As yet only two compounds of cyanogen with chlorine are known, the elementary composition of which is exactly the same, while their properties are wholly different, one of the compounds being gaseous at the ordinary temperature of our climate, and the other solid and boiling only at about  $390^{\circ}$ . The gaseous chloride of cyanogen  $\text{CyCl}$  or  $\text{C}_2\text{NCl}$  is obtained by causing chlorine to act on moist cyanide of mercury, which reaction is expressed by the following equation:



It is also prepared by passing a current of chlorine through a concentrated solution of cyanohydric acid, when the gaseous chloride of cyanogen remains in solution, and may be disengaged by gently heating the liquid, the gas being dried by passing it over chloride of calcium. It is a colourless gas, of a strong odour, causing tears, liquefying at about  $10.4^{\circ}$ , and solidifying at  $-0.4^{\circ}$ . Thus, this substance passes through three states in a very small change of temperature. Water dissolves about 25 times its vol., and alcohol and ether 50 times its vol. of it. Liquid chloride of cyanogen soon passes into the solid modification, called *solid chloride of cyanogen*. If, in fact, it be enclosed in a glass tube hermetically sealed, it undergoes at first no change, and if the tube be broken, it is wholly evolved in the gaseous state, while, in a few days, long prismatic crystals, ultimately occupying the whole mass, will be found to be developed. If the tube be then broken, no gas is

disengaged, and we find only crystals melting at  $284^{\circ}$ , and boiling at  $374^{\circ}$ . Solid chloride of cyanogen is directly formed, when anhydrous prussic acid is poured into a large bottle filled with dry chlorine and exposed to the sun. The density of the vapour of solid chloride of cyanogen is three times greater than that of the gaseous chloride, for which reason the formula  $\text{CyCl}$  has been assigned to the gaseous chloride, and the formula  $\text{Cy}_3\text{Cl}_3$  to the solid. The equivalents of these substances are therefore represented by 4 gaseous volumes.

The two chlorides of cyanogen combine directly with ammoniacal gas, and form solid compounds, of which the formulæ are,

For the gaseous chloride.....  $2\text{NH}_3, \text{CyCl}$ .  
 “ solid chloride.....  $3\text{NH}_3, \text{Cy}_3\text{Cl}_3$ .

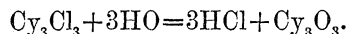
The first is soluble in water, and the second is insoluble.

Two compounds of cyanogen with bromine and iodine are also known.

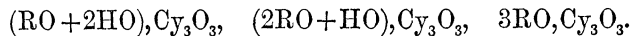
#### COMPOUNDS OF CYANOGEN WITH OXYGEN.

§ 1504. Four isomeric compounds of cyanogen and oxygen are known, *cyanic acid*, *cyanuric acid*, *cyamelide*, and *fulminic acid*, the first two of which appear to present the same relations of constitution as the gaseous and solid chlorides of cyanogen.

By digesting solid chloride of cyanogen with water, chlorohydric acid and a solid white substance, cyanuric acid  $\text{Cy}_3\text{O}_3$ , are formed :



The same compound is found under many other circumstances, and particularly when certain substances of animal origin are decomposed. A solution of the substance in hot water again deposits it, on cooling, in crystals, which are hydrated and present the formula  $\text{Cy}_3\text{O}_3, 7\text{HO}$ , while, when dried at  $212^{\circ}$ , the formula becomes  $\text{Cy}_3\text{O}_3, 3\text{HO}$ ; that deposited from a nitric or chlorohydric solution also presenting the latter composition. The 3 equiv. of water are basic, and may be replaced partially or wholly by an equivalent quantity of base; and, in fact, three series of cyanides are known, of which the general formulæ are



Cyanuric is therefore a tribasic acid.

Cyanuric acid, heated in a small glass retort, passes over wholly in distillation, but is then deeply changed, for the distilled product forms a very volatile liquid, of an odour resembling concentrated acetic acid, and which reddens litmus and behaves like a powerful acid. Its composition is the same as that of cyanuric acid dried at  $212^{\circ}$ , but it forms only one series of salts, and should be considered as a monobasic acid. The formula  $\text{CyO}, \text{HO}$  has been

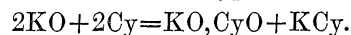
assigned to this acid, called *cyanic*, and to its salts the general formula  $\text{RO}, \text{CyO}$ .

Cyanic acid is spontaneously converted into an isomeric substance, called *cyamelide*, while the transformation does not take place so long as the cyanic acid is kept at a very low temperature; but, at the ordinary temperature, the liquid soon becomes clouded, while at the same time its temperature rises spontaneously, and it is converted into a solid mass, resembling porcelain. This is cyamelide, a wholly neutral substance, insoluble in water, alcohol, and ether, and which reproduces the original cyanic acid by distillation.

Cyanic acid may also be transformed, directly, into cyanuric acid, by adding a small quantity of nitric or acetic acid to a concentrated solution of cyanate of potassa, which converts the salt into cyanurate.

Cyanic acid may be prepared, directly, in several ways:

1. By passing cyanogen gas through a solution of potassa or carbonate of potassa, cyanate of potassa and cyanide of potassium are formed, the reaction being similar to that of chlorine on alkaline lixivæ, when it converts them into hypochlorites, (§ 450):



2. By heating a mixture of prussiate of potash and nitrate of potassa or peroxide of manganese, when cyanic acid passes over in distillation. The mixture may also be roasted in the air, and then treated with boiling alcohol, which dissolves the cyanate of potassa.

3. By fusing yellow prussiate of potash at a red-heat, and throwing litharge into the melted mass as long as the former is reduced. Boiling alcohol then dissolves the cyanate of potassa formed.

The fourth isomeric modification of cyanic acid, *fulminic acid*, is formed under quite peculiar conditions. Mercury or silver being treated with a mixture of alcohol and nitric acid, a very powerful reaction ensues, and various products of the oxidation of alcohol pass into the receiver, among which may be distinguished aldehyde, acetic acid, formic acid, and nitrous, acetic, and formic ethers. A crystalline salt, which is the *fulminate of mercury* or *silver*, is deposited in the retort.

The composition of fulminic acid is the same as that of cyanic and cyanuric acids, but it is a bibasic acid, the formula of which should be written  $\text{Cy}_2\text{O}_3, 2\text{HO}$ , since it forms, in fact, two series of salts, of which the general formulæ are  $(\text{RO} + \text{HO}), \text{Cy}_2\text{O}_3$  and  $2\text{RO}, \text{Cy}_2\text{O}_3$ . The formulæ of the fulminates of mercury and silver are  $2\text{HgO}, \text{Cy}_2\text{O}_3$  and  $2\text{AgO}, \text{Cy}_2\text{O}_3$ ; and by treating the fulminate of silver with potassa, only one-half of the silver is precipitated, while a double fulminate, of the formula  $(\text{AgO} + \text{KO}), \text{Cy}_2\text{O}_3$ , is obtained.

The dry fulminates detonate with extreme violence, either by percussion or when heated. Fulminate of mercury is used in the manufacture of percussion caps for firearms.

They are prepared on a large scale, by dissolving 1 part of mercury in 12 of nitric acid of a density of 1.36, adding to the solution 11 parts of alcohol at 0.80, and then gently heating the mixture in a distilling apparatus, in order to condense the disengaged volatile products, which may be used in another operation. The liquid remaining in the retort deposits the fulminate on cooling.

*Metallic Sulphocyanides and Sulphocyanohydric Acid.*

§ 1505. By heating to a dull-red an intimate mixture of 2 parts of prussiate of potash and 1 part of sulphur, and then treating it with boiling alcohol, *sulphocyanide of potassium*  $\text{KS, CyS}$  is deposited in small crystalline aciculæ; and it may be regarded as a cyanate of potassa, in which the oxygen of the acid and the base is replaced by a corresponding quantity of sulphur. A larger quantity is obtained by heating 46 parts of prussiate of potash, 17 parts of carbonate of potassa, and 16 of sulphur, and treating the mass with boiling alcohol.

If sulphocyanide of potassium be distilled with phosphoric acid, *sulphocyanohydric acid*  $\text{CyS, HS}$  is obtained, a large proportion of which is, however, decomposed. Acetate of lead may also be poured into the solution of the sulphocyanide of potassium, when sulphocyanide of lead  $\text{PbS, CyS}$  is precipitated, and is decomposed by sulphydric acid, a colourless acid liquor, reddening litmus, being formed.

Free sulphocyanohydric acid, and the alkaline sulphocyanides, yield, with sesquisalts of iron, precipitates of a blood-red colour, which reaction is often used to detect these salts.

By pouring into a solution of an alkaline sulphocyanide, 6 or 8 times its volume of concentrated chlorohydric acid, a deposit of small white aciculæ is formed, which are to be washed with a small quantity of cold water. It is a new acid, called *persulphocyanohydric*, of the formula  $\text{CyS}_2\text{, HS}$ . This acid may be dissolved in boiling water, and is deposited from it, on cooling, in small crystalline aciculæ. It is a feeble acid, which combines directly, without alteration, under certain conditions, while under other conditions it is decomposed. Persulphocyanohydric acid, and sulphocyanohydrate of ammonia, yield, when heated, a great number of new substances, as yet but imperfectly known.

## ESSENTIAL OILS.

§ 1506. A large number of volatile substances, possessing generally a powerful and frequently an agreeable odour, adapting them for the toilet, are extracted from vegetables; and the greater portion of them are liquid, while some are solid at the ordinary temperature. These substances are in general prepared by expressing the juice of the vegetables which contain them, and distilling it with water, when the essential oil passes over with the water, and, as it is generally less volatile than the latter, the proportion which passes over, compared with the quantity of water, is the greater as the difference between the boiling point of water and that of the oil is less. Parts of the vegetables themselves, the flowers for example, are frequently distilled with water, and when the essential oil is lighter than water, the products are collected in a bottle of peculiar

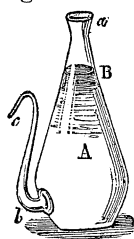


Fig. 684.

shape, (fig. 684,) called a *florence receiver*. The bottle is conical, and has a lateral tube communicating with the bottom, and of which the orifice is at a lower level than the mouth *a* of the bottle. The water and oil distilled pass into the bottle through the mouth *a*, the oil forming the upper stratum; and when the bottle is filled above the level of the orifice *c*, the water escapes through the latter, and the essential oil floats on its surface, in a layer of a thickness in proportion to the diameter of the neck of the bottle, and which is removed from time to time with a pipette. An ordinary alembic is used for distillation, but the vegetables subjected to the operation must not be allowed to reach a temperature above  $212^{\circ}$ , in order to avoid the generation of empyreumatic products, which, distilling at the same time as the essential oil, would injure its flavour. In order to prevent these accidents, the vegetables are placed in bags, or metallic vessels pierced with holes, and kept above the liquid in the cucurbit, in the space traversed by the vapour.

As the water which has distilled over with the essential oil generally dissolves a small quantity of it, sufficient to impart to it its odour, it is carefully collected and sold. Thus, while distilling orange-flowers with water, a certain quantity of *essence of orange-flower* collects at the top of the florence receiver, while a water, possessing a very agreeable smell, and which is sold under the name of *orange-flower water*, is found under it.

The quantity of essential oil which exists in the portions of vegetables subjected to distillation is frequently so small that no separate oil can be obtained, but only an odoriferous water. The same

thing occurs when the boiling point of the essential oil is very high; and in the latter case, the fresh water in the cucurbit is replaced by water saturated with salt, which boils at  $230^{\circ}$ , and the vessel containing the flowers is suspended in this water; when the tension of the vapour of the oil is necessarily greater in this hotter space, and a larger quantity of it passes over.

Some essential oils would be very easily injured by heat, and at other times the flowers in which they exist contain alterable principles, and the distilled oil is far from possessing the odour of the flower. They are then not distilled, and we are satisfied with separating the oil by dissolving it in a fixed oil, of itself inodorous, poppy-oil for example; for which purpose the flowers are spread thinly over woollen cloths soaked in poppy-oil, when the cloths are piled on each other, and the whole placed under a press.

Essential oils differ materially from each other, both in their composition and chemical reactions; and, if due regard be paid to the nature of the compounds from which they are derived, we are led to divide them among those series most differing from organic bodies. A great number of oils contain only carbon and hydrogen, while others also contain oxygen, and, lastly, some few contain sulphur. We shall therefore divide them into three groups, and include in the first, those oils which are composed of hydrogen and carbon alone; in the second, those which contain, in addition, oxygen; and in the third, the sulphuretted essential oils.

#### HYDROCARBURETTED ESSENTIAL OILS.

§ 1507. The composition of the greater number of these oils corresponds to the formula  $C_5H_8$ , and we therefore here find a great number of isomeric substances, the chemical properties of which are so similar that recourse must be had to very delicate characters to prove their non-identity. The mobility of their molecular constitution is such, that by distilling, or forming them into compounds from which they are subsequently separated, their nature is changed.

#### *Essential Oil of Terpentine or Terebenthene* $C_{20}H_{16}$ .

§ 1508. This is the most important of the essential oils, on account of its application in the arts, being used in the preparation of varnishes, and, in general, as a solvent for certain substances, which it deposits, by spontaneous evaporation, on the surface of bodies coated with the solution.

A viscous substance, called *terpentine*, consisting essentially of a resin, *colophony*, or common resin dissolved in oil of terpentine, exudes from the trees of the family of the coniferæ, chiefly from the pines. By distilling terpentine with water, the greater portion of the essential oil is carried over by the vapour of water, in which state it still contains a small quantity of resin, partly formed by the oxidation of the oil by contact with the air. In order to purify it, it is again distilled with water, dried by leaving it for some time over



chloride of calcium, and again distilled for the last time by itself, avoiding as much as possible the contact of the air.

The essential oil extracted from the various terpenes of commerce is far from being identical, and appears to vary according to the tree which has produced it. French oil of terpentine, produced by the *pinus maritima* which grows in the south of France, is a colourless, very volatile liquid, of a characteristic smell and an acrid and burning taste. Its density at  $32^{\circ}$  is 0.875, while the density of its vapour is 4.76; and if it be admitted that its equivalent is represented by 4 volumes of vapour, like that of the carburetted hydrogen hitherto described, its formula should be written  $C_{20}H_{16}$ . Oil of terpentine, which we shall call, for brevity's sake, *terebenthen*,\* boils at about  $300^{\circ}$ , the boiling point being rarely constant. It deviates polarized light to the left, while the various oils differ from each other in the intensity of their rotatory power; some even producing deviation to the right, as the oil extracted from the *pinus tada* of Carolina, which is chiefly used in England. Moreover, the same *terebenthen* does not maintain an identical rotatory power when it is subjected to successive distillations, and its molecular constitution appears to be modified by the simple process of distillation; these modifications being much more decided when the distillation is effected under high pressure, and, consequently, at a more elevated temperature. An oil of terpentine having been kept boiling, for several hours, under a pressure of 8 or 10 atmospheres, more than one-half of it was converted into an isomeric product which did not boil under  $464^{\circ}$ .

*Terebenthen* dissolves but slightly in water, communicating to it, however, its characteristic odour; and it dissolves freely in alcohol, ether, and the fixed oils. It dissolves a large proportion of sulphur, phosphorus, and several organic compounds.

§ 1509. *Terebenthen*, left for a long time in contact with water, deposits colourless crystals, which have been improperly called *hydrate of terebenthen*, because their composition corresponds to the formula  $C_{20}H_{16}.6HO$ . A much larger quantity of this compound is obtained by leaving a mixture of 8 parts of oil of terpentine, 2 parts of ordinary nitric acid, and 1 part of alcohol at 0.80, to itself for several months, during which time it is frequently shaken; when a crystalline magma is formed, which is expressed between tissue-paper, and redissolved in boiling water, from which it is deposited in small prismatic crystals on cooling. By redissolving it in boiling alcohol, it yields large crystals, which melt at  $217.4^{\circ}$ , while, at a more elevated temperature, they lose 2 equivalents of water, and form a new *hydrate*  $C_{20}H_{16}.4HO$ , which distils at about  $482^{\circ}$  without change. The density of its vapour being 6.26, the equivalent  $C_{20}H_{16}.4HO$  is represented by 2 volumes.

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\* Called *Camphine* in the U. S., when purified by distillation.—J. C. B.

§ 1510. Terebenthen combines readily with chlorohydric acid gas, and absorbs large quantities of it, with elevation of temperature, the saturated liquid depositing crystals, on cooling, varying in proportion according to the nature of the oil, and which are purified by recrystallization in boiling alcohol. The crystals melt at  $302^{\circ}$ , the substance boiling at about  $338^{\circ}$ , with partial decomposition; and its composition corresponds to the formula  $C_{20}H_{18}HCl$ , showing it to be a *chlorohydrate of terebenthen*, which is sometimes called *artificial camphor*: it deviates the plane of polarization to the left. The liquid which floats on the crystals, in the preparation of artificial camphor, is itself a *liquid chlorohydrate of terebenthen*, of the same composition as the solid chlorohydrate, but which does not solidify at any temperature.

If solid chlorohydrate of terebenthen be passed over caustic lime heated to redness, a liquid carburetted hydrogen separates from it, having the same composition and boiling point as the original terebenthen, but differing from it by exerting no action on polarized light: it has been called *camphilen*. It also combines with gaseous chlorohydric acid, yielding, at the same time, a solid and a liquid chlorohydrate; and it is therefore composed of at least two distinct liquids, like terebenthen itself. By decomposing the liquid chlorohydrate of terebenthen by means of lime, an essential oil is separated having no action on polarized light, and yielding only liquid chlorohydrate with chlorohydric acid, which new oil has been called *terebilen*. Bromohydric and iodohydric acids produce compounds similar to those of chlorohydric acid.

§ 1511. Terebenthen undergoes very curious isomeric modifications by contact with sulphuric acid. By mixing, in a well-cooled flask, oil of turpentine with about  $\frac{1}{20}$  of its weight of sulphuric acid, and leaving the mixture to itself during 24 hours, shaking it frequently, a red and viscous liquid is obtained; and after allowing it to rest for some time, the supernatant oil is decanted, when a black residue, saturated with acid, remains in the flask. If the decanted oil be distilled, a small quantity of sulphurous acid first passes over, and then an essential oil, having the same composition, density, and boiling point as terebenthen, but differing from it in exerting no rotatory power on polarized light, and in forming with chlorohydric acid gas a compound of the formula  $2C_{20}H_{18}HCl$ , which consequently contains one-half less chlorohydric acid than the chlorohydrate of terebenthen. This essential oil has been called *tereben*.

The essential oil modified by sulphuric acid is not solely composed of *tereben*, and when it has separated by distillation, and the temperature is raised to  $590^{\circ}$ , a new product is obtained, composed of a viscous oil, which is bleached by being distilled over an alloy of potassium and antimony, (§ 1017). This liquid is highly *dichroic*; light which passes through it normally being colourless, while that

obliquely refracted by it, particularly at certain angles of incidence, exhibits a beautiful indigo colour. Its density is 0.940 at 48.2°, and it has no rotatory power. It absorbs chlorohydric acid gas, but without forming any fixed compound, for carbonate of lime readily abstracts the chlorohydric acid. The name of *colophen* has been given to this gas, the composition of which is the same as that of terebenthen; and large quantities of it are obtained by the direct distillation of resin.

Chlorine acts powerfully on terebenthen and its isomeric compounds, chlorohydric acid being disengaged, while a viscous, colourless liquid is formed, having the smell of camphor, and which is *quadrichlorinated terebenthen*, its formula being  $C_{20}H_{12}Cl_4$ .

*Oil of Lemons, or Citrene*  $C_{30}H_{18}$ .

§ 1512. Lemon-peel contains an agreeable-smelling essential oil, of an identical composition with terebenthen, and which we shall call *citren*. It may be extracted by expressing the yellow part of the lemon peel, but it is more generally separated by distilling the peel with water, in which case the smell of the oil is, however, less grateful. Citren boils at about 338°, and its density is 0.847 at 71.6°, while the density of its vapour is the same as that of terebenthen, for which reason it has received the same formula  $C_{20}H_{16}$ ; but it polarizes to the right. It combines with chlorohydric gas forming a liquid and a solid chlorohydrate having the same composition. These *chlorohydrates of citren* contain twice as much chlorohydric acid as the chlorohydrate of terebenthen, and their formulæ is therefore  $C_{20}H_{16}, 2HCl$ .

*Oil of Oranges, or Oil of Neroli*  $C_{20}H_{16}$ .

§ 1513. Orange-peel, like lemon-peel, contains an essential oil, to which it owes its fragrance, and of which the formula  $C_{20}H_{16}$  is the same. It yields, with chlorohydric acid, a solid and a liquid product, of an identical composition with the chlorohydrates of citren; and it polarizes to the right.

In the bergamot, in juniper-berries, in the seeds of parsley, and many other vegetables, essential oils of the composition  $C_5H_4$  are found, but which are distinguished by certain chemical properties, and by their rotatory powers, from the essential oils just described. Essential oils of bergamot, Seville oranges, cedrat, caraway, and limes rotate toward the right. Essential oils of the same composition are obtained in the distillation of several organic substances. Certain kinds of bitumen yield a yellowish liquid, *petrolen*, which may be made perfectly colourless by distilling it over potassium, and presenting the same composition with oil of turpentine. But as it boils at 536°, and the density of its vapour is double, its formula should be written  $C_{40}H_{32}$ .

## OXYGENATED ESSENTIAL OILS.

§ 1514. These oils being numerous, and their chemical properties very various, we shall describe only the most important and best known of them.

## CAMPHORS.

§ 1515. The name of *camphors*, or *stearoptens*, has been given to neutral compounds, solid at the ordinary temperature, volatile, having an odour resembling those of ordinary camphor, and applicable to the same uses. We shall here treat only of the camphor from Japan and that from Borneo.

*Japan Camphor*  $C_{20}H_{16}O_{20}$ .

§ 1516. Japan camphor is extracted from the *laurus camphora*, the wood of which tree contains it so abundantly that small crystals of it are seen in the fissures. The trunk and branches are split into small pieces and distilled with water in iron boilers, covered with an earthen capital filled with straw or small twigs, on which the camphor sublimes and crystallizes in the shape of *crude camphor*. It is distilled with a small quantity of lime and charcoal in flat-bottomed vessels, resembling those used for the sublimation of chlorohydrate of ammonia, (§ 516,) when the camphor sublimes at the upper part, and forms crystalline, colourless, and transparent masses, such as are found in commerce. At the ordinary temperature, the tension of the vapour of camphor is very feeble, and, nevertheless, it exhales an intense and characteristic odour; while, when kept in a close-stoppered bottle, the vapour condenses on its sides, and forms small brilliant crystals, remarkable for their sharpness. Camphor melts at  $347^{\circ}$ , and boils at about  $410^{\circ}$ , its density being 0.986, and the density of its vapour 5.32. From its great elasticity it is very difficult to pulverize. Its chemical composition corresponds to the formula  $C_{10}H_8O$ , which is generally written  $C_{20}H_{16}O_2$ ; its equivalent then corresponding to 4 volumes of vapour. Camphor is slightly soluble in water, but dissolves more freely in alcohol, ether, and concentrated acetic acid, and it burns with a white and smoky flame. Camphor obtained from the family of the laurels, when dissolved in alcohol, rotates toward the right.

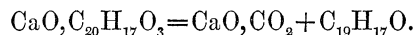
Chlorine does not act readily on camphor, but when dissolved in chloride of phosphorus  $PCl_3$ , and subjected to the action of chlorine, it yields *chlorinated camphor*  $C_{20}H_{10}Cl_6O_2$ , which is separated from the perchloride of phosphorus by washing it with water and weak solutions of carbonate of potassa.

Camphor absorbs chlorohydric acid gas, and yields a colourless liquid of the formula  $C_{20}H_{16}O_2.HCl$ , which is readily destroyed by water, while camphor separates from it.

§ 1517. Alkaline solutions exert no action upon camphor, but if its

vapour be passed over potassic lime heated to  $750^{\circ}$  in a glass tube, an acid called *campholic* is formed, which combines with the alkaline substance, and which is then separated by dissolving in water and supersaturating with chlorohydric acid. The precipitated camphoric acid is dissolved in a mixture of alcohol and ether, from which it separates in crystals, melting at  $176^{\circ}$ , and boiling at  $482^{\circ}$ . It is insoluble in water, but very soluble in alcohol and ether. When crystallized, its formula is  $C_{20}H_{18}O_4$ , or more properly  $C_{20}H_{17}O_3 \cdot HO$ , which corresponds to 4 volumes of vapour, for the density of the vapour of campholic acid is 5.9. The formula of campholic acid differs from that of camphor only by containing, in addition, the elements of 1 equiv. of water. The formula of campholate of silver is  $AgO, C_{20}H_{17}O_3$ .

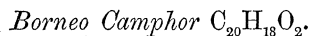
Campholate of lime  $CaO, C_{20}H_{17}O_3$  is decomposed by heat into carbonate of lime and a peculiar liquid called *campholone*  $C_{19}H_{17}O$ .



Campholic acid, distilled with anhydrous phosphoric acid, gives off water and carbonic acid, while a carburetted hydrogen  $C_{13}H_{16}$ , called *campholen*, which boils at  $275^{\circ}$ , is formed.

§ 1518. Cold nitric acid dissolves camphor, and parts with it when diluted with water, while, by the application of heat, a peculiar acid, called *camphoric*, is developed. In order to prepare this acid, camphor is boiled for a long time with 10 times its weight of nitric acid, and as the latter distils over, it is collected and poured back into the retort. At the close of the operation, the excess of nitric acid is driven off by evaporation, when the camphoric acid separates in a crystalline mass, which is purified by dissolving it in carbonate of potassa, and again separating it by means of nitric acid. Camphoric acid is moderately soluble in boiling water, the greater portion of it separating during cooling, while alcohol and ether dissolve it readily. Its composition corresponds to the formula  $C_{20}H_{16}O_8$ ; and the camphor, by being converted into camphoric acid, combines therefore with 6 equiv. of oxygen, which it takes from the nitric acid. The formula of camphoric acid should be written  $C_{20}H_{14}O_6 \cdot 2HO$ , because it is a bibasic acid, and the general formula of its salts is  $2RO, C_{20}H_{14}O_6$ . When heated it is decomposed into water and a crystallized substance, boiling at  $518^{\circ}$ , which, from its composition  $C_{20}H_{14}O_6$ , may be regarded as *anhydrous camphoric acid*. Camphoric acid, dissolved in alcohol, rotates toward the right.

§ 1519. A species of camphor is extracted from the labiates, which, in its chemical composition, appears identical with the camphor of the laurels, but which rotates toward the left.



§ 1520. From the *dryabalanops camphora* exudes a more or less viscous oil, containing a crystallizable substance, of which the pro-

perties are analogous to those of Japan camphor. It has been called *Borneo camphor*, and is often found crystallized in old trunks of the tree of the *dryabalanops camphora*. The camphor imported from Borneo and Sumatra is in small, crystalline, colourless, and transparent fragments, insoluble in water, but dissolving freely in alcohol and ether. It melts at about  $383^{\circ}$ , and boils at about  $419^{\circ}$ . Borneo camphor differs from Japan camphor only by containing 2 additional equiv. of hydrogen, which are consumed by heating it with nitric acid; the Borneo being converted into Japan camphor. The liquid portion of the essential oil of the *dryabalanops camphora* is essentially composed of a liquid carburetted hydrogen  $C_{20}H_{16}$ , called *bornëen*, boiling at about  $320^{\circ}$ , and isomeric with oil of turpentine, similarly to which it polarizes to the left, its rotatory power being much greater. Nitric acid, after some time, and assisted by gentle heat, converts bornëen into Japan camphor, probably by the mere absorption of oxygen.

*Of some other Stearoptens analogous to Camphor.*

§ 1521. Stearoptens, exhibiting properties analogous to the camphors, are found in a great number of vegetables; but we shall only mention them, for as yet they possess but little interest, and are but little known.

Peppermint contains a stearopten of the formula  $C_{20}H_{20}O_2$ , called *menthen*  $C_{20}H_1$ , which boils at  $325.4^{\circ}$ . Oil of mint rotates toward the right.

Oil of cedar is composed of a crystallizable substance  $C_{32}H_{26}O_2$ , and a liquid carburetted hydrogen, *cedren*  $C_8H_{24}$ , which boils at  $478.4^{\circ}$ .

Oil of absinth, when purified, boils at  $399.2$ , and rotates toward the right: its formula being  $C_{20}H_{16}O_2$ , it is isomeric with Japan camphor.

The root of elecampane (*inula helenium*) contains a white crystallizable substance, *helenin*, very soluble in alcohol and ether, melting at  $161.6^{\circ}$ , boiling at about  $536^{\circ}$ , and presenting the formula  $C_{42}H_{28}O_6$ .

An essential oil, composed of a liquid portion and a portion which solidifies at  $9.5^{\circ}$ , is extracted from roses; but the composition of the two substances is not exactly known.

Oil of lavender contains a considerable proportion of Japan camphor, and a volatile oil, the essential oil properly so called, which has been used in the arts.

BENZOIC SERIES.

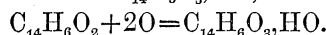
*Oil of Bitter Almonds*  $C_{14}H_6O_2$ .

§ 1522. Bitter almonds contain an essential oil, and a non-volatile fatty oil, which latter is expressed by subjecting them to pressure; and if the pulp moistened with water be then distilled in an

alembic, a volatile oil, which falls to the bottom of the receiver, passes over with the water. This is the *oil of bitter almonds*, mixed with cyanohydric acid and two new substances, *benzoin* and *benzoic acid*, which shall soon be described. They are separated by distilling the crude oil with lime and protosulphate of iron, reduced to a paste with water; the distilled oil being removed with a pipette, and again distilled in a glass retort, collecting separately the first portions, which contain water.

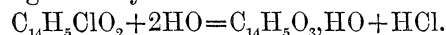
Oil of bitter almonds is a colourless, very fluid liquid, having a peculiar odour resembling that of cyanohydric acid; and its density is 1.043, while it boils at  $348.8^{\circ}$ . Water dissolves about  $\frac{1}{80}$  of its weight of it, while it is indefinitely soluble in alcohol and ether. Its formula is  $C_{14}H_6O_3$ , and it exerts no rotatory power.

Oil of bitter almonds rapidly absorbs the oxygen of the air, and is converted into benzoic acid  $C_{14}H_5O_3, HO$ ,



Anhydrous benzoic acid is therefore derived from the oil of bitter almonds, by the substitution of 1 equivalent of oxygen in the place of 1 equivalent of hydrogen. Benzoic acid is also formed when oil of bitter almonds is boiled with a solution of potassa; the hydrated potassa converting, at a high temperature, the oil of bitter almonds wholly into benzoic acid, hydrogen being at the same time disengaged. Chlorine, in contact with water, effects the transformation in a very short time.

§1523. Dry chlorine acts powerfully on oil of bitter almonds, disengaging chlorohydric acid. When the evolution of the gas has ceased, the liquor is heated to drive off the dissolved chlorine, and a liquid of a penetrating and disagreeable odour is obtained, of the density 1.106, and boiling at  $383^{\circ}$ , which is *monochlorinated oil of bitter almonds*  $C_{14}H_5ClO_2$ . Water, particularly when hot, decomposes it, forming chlorohydric and benzoic acids:



It has not yet been ascertained if the oil of bitter almonds forms still more chlorinated products with chlorine. Bromine converts it into *monobrominated oil*  $C_{14}H_5BrO_2$ ; and *monoiodinated oil*  $C_{14}H_5IO_2$  is obtained, crystallized in laminæ, by distilling the monochlorinated oil over iodide of potassium. By replacing the iodide of potassium by sulphide of lead, or cyanide of mercury, a *monosulphuretted oil*  $C_{14}H_5SO_2$ , or a *monocyanuretted oil*  $C_{14}H_5CyO_2$ , is obtained. Some chemists take a different view of the composition of these various bodies, and admit the existence of an hypothetical radical  $C_{14}H_5O_2$ , called *benzoyl*, which, combined with hydrogen, constitutes the oil of bitter almonds  $C_{14}H_5O_2, H$ , thus forming a *hydruret of benzoyl*, while benzoic acid is the oxide of benzoyl  $C_{14}H_5O_2, O$ . The chlorinated, brominated, cyanuretted, and sulphuretted oils are *chlorides*, *bromides*, *sulphides*, and *cyanides of benzoyl*.

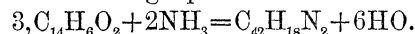
§ 1524. The chlorinated oil of bitter almonds absorbs a large quantity of ammoniacal gas, and is converted into a white crystalline compound  $C_{14}H_7NO_2$ , or *benzamide* :



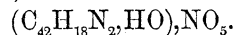
By treating the solid product of the reaction with water, the ammoniacal salt which formed during the operation is dissolved, while the benzamide alone remains, and may be crystallized from its solution in alcohol. The relation of benzamide  $C_{14}H_5O_2, NH_2$  with the benzoate of ammonia  $(NH_3, HO), C_{14}H_5O_3$  is the same as that of sulphamide  $SO_3, NH_2$  with sulphate of ammonia  $(NH_3, HO), SO_3$ .

Benzamide dissolves in boiling water, and separates from it, on cooling, in crystals, which melt at  $239^\circ$ , and boil without change at a higher temperature. Benzamide, treated with a cold alkaline lye, undergoes no change, while at the boiling point it yields benzoate of potassa and ammonia. Sulphuric acid also decomposes it, sulphate of ammonia and benzoic acid being formed.

§ 1525. The oil of bitter almonds, kept for several weeks at a temperature of  $100^\circ$  to  $120^\circ$ , with 20 times its volume of an aqueous solution of ammonia, gives rise to a large number of crystals, which are obtained isolated by removing the unaltered oil by ether. They are dissolved in cold alcohol, which, by evaporation, deposits them in a pure state, when their composition is represented by the formula  $C_{42}H_{18}N_2$ . It has been called *hydrobenzamide*, and its formation is represented by the following equation :



Hydrobenzamide, dissolved in alcohol, is readily converted, by boiling, into ammonia and oil of bitter almonds. If hydrobenzamide be boiled with a solution of caustic potassa, crystalline flakes are formed, which, by recrystallization in alcohol, furnish colourless crystals of the formula  $C_{42}H_{18}N_2$ , like that of the original hydrobenzamide, but which differ from it widely in its properties. This new substance, called *amarin*, is a true organic base, which forms crystallizable salts with the acids. The formula of chlorohydrate of amarin is  $C_{42}H_{18}N_2, HCl + HO$ , while that of the nitrate, which is but slightly soluble in water, is



§ 1526. By adding chlorohydric acid to water which has distilled with the oil of bitter almonds in the preparation of the latter substance, and evaporating it to dryness at a gentle heat, the residue is composed of chlorohydrate of ammonia, and a peculiar substance, called *formobenzoylic acid*, which is removed by dissolving it in ether, when it is deposited after evaporation in the form of crystalline spangles, having the smell of bitter almonds and a strongly acid reaction. This substance dissolves readily in water, alcohol, and ether, and its composition corresponds to the formula  $C_{10}H_8O_6$ , or rather  $C_{10}H_7O_5, HO$ , the equivalent of water being



replaced, in the salts, by 1 equivalent of base. The formula of the acid may be written  $C_{14}H_8O_2, C_2HO_4, HO$ , which would represent it as formed by the combination of 1 equivalent of oil of bitter almonds and 1 equivalent of formic acid; and such, in fact, is the constitution assigned to it by its behaviour in a great number of chemical reactions: thus, with oxidizing reagents, it yields carbonic acid, produced by the combustion of the formic acid and oil of bitter almonds.

*Benzoic Acid*  $C_{14}H_8O_3, HO$ .

§ 1527. Oil of bitter almonds rapidly absorbs the oxygen of the air, and is converted into benzoic acid  $C_{14}H_8O_3, HO$ , which same transformation is effected by exposing the oil to oxidizing reagents. Benzoic acid is also extracted from a large number of vegetable and animal substances, in which it generally does not exist already formed, being the product of chemical reactions. In the laboratory it is obtained from the resin of benzoin, by various processes, the most simple of which consists in placing in an earthen or cast-iron capsule 1 kilog. of coarsely powdered benzoin, covering the capsule with a sheet of tissue-paper, the edges of which are pasted to the vessel, and then surmounting it with a pasteboard cone. The capsule being heated in a sand-bath for 3 or 4 hours, the vapours of benzoic acid condense on the sides of the cone, after having traversed the tissue-paper, which retains a small quantity of the empyreumatic oily substances, which would injure the product. This process yields very pure benzoic acid, in the form of snow-white crystals of an agreeable odour, but furnishes only a small portion of the acid which the benzoin contains; 1 kilog. of benzoin yielding only 40 gm. of benzoic acid.

By the following process, as much as 140 gm. of benzoic acid may be obtained from the same quantity of benzoin. The resin of benzoin, finely powdered, is mixed with  $\frac{1}{4}$  of its weight of carbonate of soda, and a sufficient quantity of water to make a liquid paste, which is gently heated for several hours, stirring it continually to prevent the melting of the resin. It is then heated with a larger quantity of water, to dissolve the benzoate of soda, and the benzoic acid is separated by the addition of a proper quantity of sulphuric acid.

The resin of benzoin may also be treated with 3 times its weight of alcohol at 0.75, and the benzoic acid saturated with carbonate of soda dissolved in 8 parts of water; and 2 parts of alcohol being finally added, the liquid, when decanted, is distilled in order to separate the greater portion of the alcohol. The resin which was dissolved in the alcoholic liquor separates, while the solution only contains the benzoate of soda, which is decomposed by sulphuric acid, when the benzoic acid separates almost wholly from the liquor when cool. By this method, 1 kilog. of benzoin will yield as much as 180 gm. of benzoic acid.

Benzoic acid crystallizes in lamellæ or in flexible and brilliant silky aciculæ; and it has, of itself, but little odour, while it generally preserves the smell of benzoin, particularly when it has been prepared by simple distillation. It weakly reddens litmus, melts at  $248^{\circ}$ , and boils at  $464^{\circ}$ , exhaling copious vapours already at a temperature of  $300^{\circ}$  or  $400^{\circ}$ . The density of its vapour being 4.27, its equivalent  $C_{14}H_5O_3HO$  corresponds to 4 volumes of vapour. It requires for its solution 25 parts of boiling and 200 parts of cold water, while it dissolves in 2 parts of alcohol, and is also very soluble in ether.

The general formula of the benzoates is  $RO, C_{14}H_5O_3$ . The benzoates of potassa, soda, and ammonia, are very soluble in water, and crystallize with difficulty. The benzoate of lime is very soluble in hot water, while cold water retains only about  $\frac{1}{20}$  of its weight of it. The benzoate of silver is prepared by double decomposition, by pouring a hot solution of nitrate of silver into a boiling solution of an alkaline benzoate, when the benzoate of silver  $AgO, C_{14}H_5O_3$  is precipitated, during the cooling, in the form of colourless needles.

Chlorine acts on benzoic acid when assisted by the rays of the sun, and produces chlorinated benzoic acid, retaining the principal properties and capacity of saturation of free benzoic acid, the same products being obtained by heating benzoic acid with the alkaline hypochlorites or with mixtures of chlorohydric acid and chlorate of potassa. Two chlorinated benzoic acids have been obtained in this manner:

Monochlorinated benzoic acid.....	$C_{14}H_4ClO_3, HO.$
Terchlorinated           "           " .....	$C_{14}H_2Cl_3O_3, HO.$

*Vinobenzoic Ether*  $C_4H_5O, C_{14}H_5O_3.$

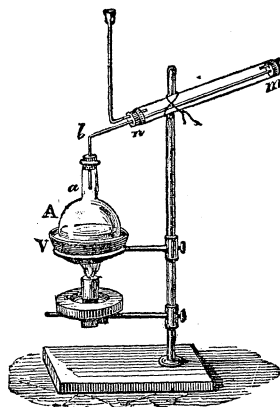


Fig. 685.

§ 1528. In order to prepare this ether, 2 parts of alcohol, 1 part of benzoic acid, and 6 parts of concentrated chlorohydric acid are heated, in a distilling apparatus, the liquid acid which distills being returned several times to the retort; when the benzoic acid is thus almost wholly converted into benzoic ether. But it is better to arrange the operation as represented in fig. 685: the mixture is placed over a water-bath in a flask A which is made to communicate with a refrigerator so arranged as to allow the distilled liquid to gradually fall back again. The liquid is treated, first with water, and then with a weak solution of carbonate of soda to remove the free benzoic

acid, after which the benzoic ether is dried by digesting it over chloride of calcium.

Benzoic ether is a colourless liquid of an oleaginous consistence, boiling at  $410^{\circ}$ , and of the density 1.054 at  $50^{\circ}$ . The density of its vapour being 5.41, its equivalent corresponds to 4 volumes of vapour, and it is insoluble in water, but soluble in all proportions in alcohol.

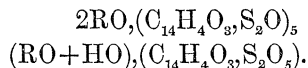
*Methylbenzoic Ether*  $C_2H_5O, C_{14}H_5O_3$ .

§ 1529. By replacing, in the preceding operation, vinic by methylic alcohol, methylbenzoic ether\* is obtained as an oily liquid, boiling at  $226.4^{\circ}$ .

*Sulphobenzoic Acid*  $(C_{14}H_4O_3, S_2O_5), 2HO$ .

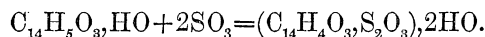
§ 1530. If vapour of anhydrous sulphuric acid be introduced into a dry and well-cooled flask containing benzoic acid, a semifluid mass is formed, which is afterward treated with water to dissolve the monohydrated sulphuric acid, and a peculiar acid, called *sulphobenzoic*, while the benzoic acid is separated unchanged. The acid liquid is saturated with carbonate of baryta, when sulphobenzoate of baryta alone remains in the liquid. By adding chlorohydric acid, crystals of *acid sulphobenzoate of baryta*  $(BaO + HO)$ ,  $(C_{14}H_4O_3, S_2O_5)$  separate, which are redissolved in boiling water and again crystallized by cooling. *Sulphobenzoic acid* may be separated by decomposing a solution of this salt with sulphuric acid added by drops: it is very soluble in water, remains undecomposed even at  $300^{\circ}$ , and may be obtained in a crystalline form by evaporation.

Sulphobenzoic acid forms two series of salts of which the general formulæ are



It is therefore a bibasic salt.

It will be seen that when benzoic acid  $C_{14}H_5O_3, HO$  is treated with anhydrous sulphuric acid, 2 equivalents of the latter enter into the new compound, but only after having parted with 1 equivalent of oxygen, which has formed water with 1 equivalent of hydrogen given off by the benzoic acid; according to the equation



*Nitrobenzoic Acid*  $C_{14}H_4(NO_4)O_3, HO$ .

§ 1531. Dilute nitric acid does not act readily on benzoic acid,

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\* More properly called *benzoic methel*.—W. L. F.

but if the fuming acid be used, and in great excess, the benzoic acid is dissolved with the disengagement of nitrous vapours, and the liquid deposits, on cooling, crystals of nitrobenzoic acid  $C_{14}H_4(NO_4)O_3.HO$ , which is purified by recrystallizations.

Nitrobenzoic acid is but slightly soluble in cold, but much more so in boiling water; and dissolves freely in alcohol and ether. If crystallized into benzoate of lime, it takes the formula



and that of baryta,  $BaO, C_{14}H_4(NO_4)O_3 + 4HO$ .

From its composition it may be admitted that the molecule of nitrobenzoic acid  $C_{14}H_4(NO_4)O_3.HO$  is merely that of benzoic acid  $C_{14}H_5O_3.HO$  in which 1 equivalent of hydrogen has been replaced by the compound  $(NO_4)$ ; and many cases will subsequently be met with in which the same substitution may be admitted.

If a current of chlorohydric acid gas be passed through an alcoholic solution of nitrobenzoic acid, *nitrobenzoic ether*  $C_4H_5O, C_{14}H_4(NO_4)O_3$  is formed, which separates in colourless crystals, fusible at  $116.6^\circ$ , and boiling at about  $570^\circ$ .

*Binitrobenzoic Acid*  $C_{14}H_3(NO_4)_2O_3.HO$ .

§ 1532. By digesting at a gentle heat 1 part of benzoic acid with 12 or 15 parts of a mixture, in equal proportions, of Nordhausen sulphuric acid and fuming nitric acid, we effect the substitution, in the molecule of benzoic acid  $C_{14}H_5O_3.HO$ , of 2 equivalents of the compound  $NO_4$  for 2 equivalents of hydrogen, and obtain binitrobenzoic acid  $C_{14}H_3(NO_4)_2O_3.HO$ .

*Bromobenzoic Acid*  $C_{14}H_5BrO_4.HO$ .

§ 1533. By introducing into a very dry bottle benzoate of silver, and bromine contained in an open tube, and leaving it to itself after having closed the bottle, the benzoate of silver absorbs the vapours of bromine, bromide of silver being formed, while the benzoic acid combines, at the same time, with the equivalent of oxygen given off by the silver and with 1 equivalent of bromine. By treating it with ether, only the new acid  $C_{14}H_5BrO_4.HO$ , dissolves, which remains in the form of a crystalline mass. It is important to remark that bromobenzoic acid has not preserved the constitution of benzoic acid, but that it is formed by the addition, and not the substitution, of new elements.

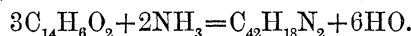
*Benzoate of Oil of Bitter Almonds.*

§ 1534. When moist chlorine is passed through oil of bitter almonds, crystals insoluble in water, but very soluble in alcohol, are, after some time, developed in it. The composition of this substance may be represented by the formula  $(2C_{14}H_6O_2, C_{14}H_5O_2)$ ; 3 molecules of the oil being grouped into one, after one of these molecules

has been converted into benzoic acid, by the oxidizing action of the moist chlorine. Its composition would therefore be analogous to that of acetal (§ 1368) and of methylal, (§ 1432.)

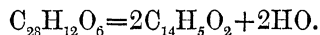
*Benzoïn*  $C_{14}H_6O_2$ .

§ 1535. If crude oil of bitter almonds be shaken with an alcoholic solution of potassa, the oil sets, in a few minutes, into a crystalline mass; the presence of a certain quantity of cyanohydric acid being necessary to the transformation. The new substance is crystallized by purifying it in alcohol. This substance, to which the name of *benzoïn* has been given, presents exactly the same composition as the oil of bitter almonds, melts at  $248^\circ$ , and may be distilled without change. Though insoluble in cold, it is slightly soluble in boiling water, and rather freely so in alcohol. Melted with hydrate of potassa, it yields benzoate of potassa. If it be left, for a long time, with an aqueous solution of ammonia, a white powder is formed, nearly insoluble in water, alcohol, and ether, which has been called *benzoïnamide*, and presents the formula  $C_{43}H_{18}N_2$ : it may be supposed to be formed by means of 3 equivalents of benzoïn  $3(C_{14}H_6O_2)$  and 2 of ammonia, from the equation



§ 1536. Benzoin dissolves when heated with nitric acid, and a new substance of the formula  $C_{14}H_5O_2$ , separates after cooling, called *benzil*, which therefore results by the simple abstraction of 1 equivalent of hydrogen from the benzoïn. The same compound is obtained when chlorine is caused to act upon benzoïn heated to fusion, when the equivalent of hydrogen is disengaged in the state of chlorohydric acid. Benzil is crystallized by purifying it in alcohol, and is a slightly yellowish substance, melting at about  $194^\circ$ .

Benzil is not changed, even at the boiling point, by an aqueous solution of potassa, while in contact with an alcoholic solution of the same alkali, it abstracts 1 equivalent of water, and is converted into an acid, called benzilic, of the formula  $C_{28}H_{12}O_6$ , which results from the combination of the elements of 2 equivalents of water with 2 equivalents of benzil:

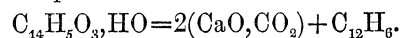


The same acid is formed by heating benzoïn with an alcoholic solution of potassa, saturating the hot solution with chlorohydric acid, and allowing it to cool, when benzilic acid is deposited in crystals. It melts at  $248^\circ$ , and decomposes at a higher temperature, giving off a certain quantity of benzoic acid.

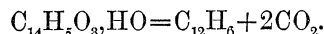
*Benzine*  $C_{12}H_6$

§ 1537. When benzoic acid  $C_{14}H_5O_3$ , HO is heated with 3 times its weight of hydrate of lime, carbonate of lime is formed, while a

colourless, very volatile liquid, of the formula  $C_{12}H_6$ , and called *benzine*, distils over, which is rectified over quicklime. The reaction is expressed by the equation



Benzine is also formed when benzoic acid in vapour is passed through a tube filled with fragments of pumice-stone and heated to redness; benzine and carbonic acid alone being formed:



Benzine is also produced by the decomposition of a great number of organic substances by heat: thus, a considerable proportion of it is found in the volatile oils formed in the manufacture of illuminating gas.

Benzine boils at  $186.8^\circ$ , and its density is 0.85, while that of its vapour is 2.38, its equivalent corresponding to 4 volumes of vapour. At  $32^\circ$  it sets into a crystalline mass, which melts only at  $44.6^\circ$ ; and it is insoluble in water, but very soluble in alcohol and ether.

Benzine is easily acted on by dry chlorine, when exposed to the rays of the sun; and if it be poured into a large well-dried bottle, filled with chlorine, and the bottle be exposed to the sun, it becomes filled with white vapours, while the sides are covered with white crystals of the formula  $C_{12}H_5Cl$ . The behaviour of this substance with an alcoholic solution of potassa leads us to write its formula  $C_{12}H_3Cl_3, 3HCl$ ; the solution, in fact, decomposing it by abstracting  $3HCl$ ; while, if the liquid be diluted with water, an oily and colourless liquid, insoluble in water, and of the formula  $C_{12}H_3Cl_3$ , separates, the density of the vapour of which being 6.37, its equivalent corresponds to 4 volumes. This is therefore *terchlorinated benzine*, and the crystalline substance formed by the direct action of chlorine on benzine may be regarded as a *terchlorinated trichlorohydrate* of benzine. This same decomposition of the crystalline compound takes place when it is distilled several times alone, or still better, over lime.

Bromine yields with benzine an analogous product  $C_{14}H_3Br_3, 3HBr$ , which, with the alcoholic solution of potassa, also produces *terbrominated benzine*  $C_{14}H_3Br_3$ .

§ 1538. Common nitric acid acts but feebly on benzine, while if it be heated with the fuming acid, it dissolves, and an addition of water precipitates from it a yellowish liquid  $C_{12}H_5(NO_4)$ , *nitrobenzine*. It may be granted that this substance is formed by the substitution of 1 equivalent of the compound  $NO_4$  for 1 equivalent of hydrogen of the benzine. Nitrobenzine solidifies at  $32^\circ$ , and melts only at  $37.4^\circ$ , while it boils at  $415.4^\circ$  without change.

By causing a large excess of fuming nitric acid to act for a long time on benzine, we can succeed in replacing 2 equivalents of hydrogen by 2 equivalents of the compound  $(NO_4)$ , and producing

*binitrobenzine*  $C_{12}H_4(NO_2)_2$ , which, by the addition of water, is precipitated in the form of a crystalline powder. By crystallization in alcohol, it is obtained in large brilliant lamellæ.

By subjecting nitrobenzine and binitrobenzine to certain reducing agents, they are converted into two very remarkable substances: *anilin*  $C_{12}H_7N$ , and *nitranilin*  $C_{12}H_6(NO_2)N$ , which are true volatile organic bases.

*Sulphobenzinic acid*  $C_{12}H_5S_2O_5HO$ , and *Sulphobenzine*  $C_{12}H_5SO_2$ .

§ 1539. Benzine is not appreciably acted on by ordinary sulphuric acid, while the anhydrous acid dissolves it with elevation of temperature, a viscous liquid being formed, which, when treated with water, deposits a crystalline precipitate, *sulphobenzine*, and produces a solution containing, with ordinary sulphuric acid, a new acid, called *sulphobenzinic*.

Sulphobenzine should be purified by crystallization in alcohol, after which it is a colourless substance, melting at  $212^\circ$ , and boiling at about  $750^\circ$ , without change. Its formula is  $C_{14}H_6SO_2$ , and the following equation expresses the reaction which produces it:



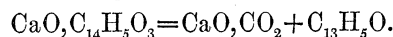
By saturating the acid liquid with carbonate of baryta, the free sulphuric acid is precipitated, and a solution of sulphobenzinate of baryta is obtained. By pouring sulphate of copper into the latter, this salt is converted into sulphobenzinate of copper, which crystallizes readily according to the formula  $CuO, (C_{12}H_5S_2O_5)$ .

When decomposed by sulphhydric acid, it produces isolated sulphobenzinic acid, a very acid liquid which may be crystallized by evaporation.

*Benzone*  $C_{13}H_5O$ .

§ 1540. When benzoate of lime is subjected *per se*, without any addition of an excess of hydrated lime, to the action of heat, with the benzine, two other products are formed: *benzone*, and a crystalline substance of which the nature is not yet known. As these two latter substances boil at much higher temperatures than benzine, they are easily separated from it, by heating the mixture to  $428^\circ$ , at which temperature the benzine is wholly volatilized. The residue being cooled to  $-4^\circ$ , nearly all the solid substance is deposited, and the benzone, which remains fluid, may be decanted.

Benzone is an oily liquid of the formula  $C_{13}H_5O$ , the reaction from which it arises being expressed by the equation



AMYGDALIN  $C_{20}H_{27}N_2O_{22}$ .

§ 1541. Bitter almonds do not contain the oil of bitter almonds

ready formed, but in its stead a very remarkable substance, called *amygdalin*, which is converted in the oil by the action of a second substance, called *emulsin*. In order to prepare amygdalin, bitter almonds are subjected to very heavy pressure, when a fatty, colourless, non-volatile oil exudes, called *oil of sweet almonds*, because it also exists in this species of almond. The balance of the oil is then removed by treating the crushed cake several times with ether; after which the pulp is boiled twice with alcohol, to dissolve the amygdalin, the greater portion of the alcohol being afterward separated by distillation; when the residue deposits the amygdalin, on cooling, in crystalline lamellæ. Amygdalin dissolves readily in water, and is deposited from it in beautiful crystals, of the formula  $C_{40}H_{37}N_2O_{23} + 6HO$ ; the 6 equivalents of water being disengaged at  $248^\circ$ . It dissolves freely in boiling alcohol, but is nearly insoluble in cold alcohol. Amygdalin rotates toward the left.

When heated with a mixture of peroxide of manganese and sulphuric acid, it is decomposed into ammonia, carbonic acid, formic acid, and oil of bitter almonds, by which process it yields more than one-half of its weight of oil.

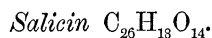
§ 1542. By pouring into a solution of amygdalin in 10 parts of water, an emulsion of sweet almonds, cyanohydric acid and oil of bitter almonds, readily known by their smell, are immediately formed. The name of *synaptase* has been given to the active substance effecting the transformation, which exists both in sweet and in bitter almonds. In order to prepare synaptase, sweet almonds, from which the oil has been previously expressed, are treated with water, and to the solution is added, first, acetate of lead in order to precipitate a gummy matter, then acetic acid to coagulate the albumen, and lastly, a large quantity of alcohol, after having precipitated the excess of lead by sulphuric acid; when synaptase is deposited in flakes, which change, on cooling, into a brittle, gum-like substance. The action of synaptase on amygdalin may be compared to that of yeast on sugars, its analogy with the phenomena of fermentation being perfect, while the products of the reaction are complicated, and a considerable quantity of sugar is formed. One part of synaptase is sufficient to decompose 10 parts of amygdalin. Synaptase is soluble in water, but it coagulates at  $140^\circ$ , and then loses all its power over amygdalin. In order to produce perfect transformation, the amygdalin must be dissolved in a large quantity of water.

From this it will be seen that, in order to prepare the oil of bitter almonds, the pulp must not be immediately distilled with water, but must be digested in the cold, or better still, at a temperature of  $86^\circ$ , long enough to allow the amygdalin to be wholly decomposed by the synaptase. The essential oil and the cyanohydric acid are then separated by distillation.



## ESSENTIAL OIL OF SPIRÆA ULMARIA, AND THE SALICYLIC SERIES.

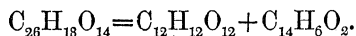
§ 1543. By distilling the flowers of the meadow-sweet (*spiræa ulmaria*) with water, an essential oil  $C_{14}H_6O_4$  is obtained, accompanied by a carburetted hydrogen, isomeric with oil of turpentine, and a crystalline substance analogous to camphor. The oil possesses acid properties, and has hence been called *spiroylous acid*, and *salicylous acid* from its correlations with a neutral substance, *salicin*, which exists in the bark of the willow. Salicin treated with a mixture of sulphuric acid and bichromate of potassa yields, in fact, a large proportion of oil of spiræa; and we shall, therefore, commence with the description of this substance, which it is impossible to separate from the series of salicylic products.



§ 1544. In order to prepare salicin, the bark of the willow is exhausted by boiling water, and litharge is added to the concentrated solution until the liquid is deprived of colour. The oxide of lead is then partially precipitated by sulphuric acid, the precipitation being finished by sulphide of barium, added by drops to prevent its being in excess. The filtered liquid is evaporated, and then deposits impure salicin, which is purified by dissolving it in water, discolouring it by animal black and recrystallizing it.

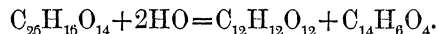
Salicin crystallizes in white inodorous aciculæ of a bitter taste, and without any reaction on vegetable colours. It loses nothing of its weight at  $212^{\circ}$ , melts at  $248^{\circ}$ , and is decomposed at a higher temperature. 100 parts of water, at the ordinary temperature, dissolve 5.6 of salicin, while boiling water dissolves it much more freely, and alcohol also dissolves it, but it is insoluble in ether. Salicin polarizes toward the left.

Cold concentrated sulphuric acid dissolves salicin, and it becomes of a blood-red colour; which reaction is a test of salicin in the bark of the willow and poplar tree. Dilute sulphuric and chlorohydric acids decompose salicin at the boiling point into glucose  $C_{12}H_{22}O_{11}$ , and a resinous substance, called *saliretin*  $C_{14}H_6O_2$ , according to the equation



§ 1545. Nitric acid forms, with salicin, very various products, according as it is more or less dilute. If 1 part of salicin be treated with 10 parts of nitric acid at  $20^{\circ}$  Baumé, and the mixture be left to itself for 1 or 2 days, shaking it frequently to hasten the solution of the salicin, a yellow liquid is obtained, which deposits a white substance, crystallized in small needles, and called *helicin*. It is very soluble in hot water, but scarcely so in cold, and its formula is  $C_{26}H_{16}O_{14} + 3HO$ , the 3 equiv. of water being given off at  $212^{\circ}$ , without alteration, while it melts at about  $347^{\circ}$ . A solution of potassa,

baryta, or ammonia decomposes it into glucose and oil of spiræa  $C_{14}H_8O_4$ :

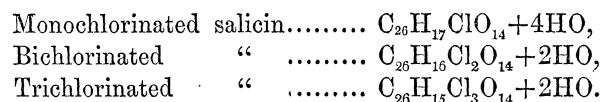


Chlorine acts readily upon helicin in the presence of water, forming *monochlorinated helicin*  $C_{26}H_{15}ClO_{14}$ , which is decomposed by a solution of potassa into glucose  $C_{12}H_{12}O_{12}$ , and into *monochlorinated oil of spiræa*  $C_{14}H_5ClO_4$ . Monobrominated helicin is prepared in the same manner, and undergoes an analogous transformation with potassa.

Beer-yeast and synaptase exert a true fermenting action on helicin, decomposing it into glucose and oil of spiræa, and producing an analogous effect on monochlorinated helicin, which they decompose into glucose, and monochlorinated oil of spiræa.

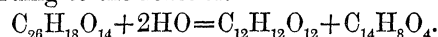
When the nitric acid is more concentrated, and it is heated, the salicin is converted into oxalic acid, and an acid which we shall describe under the name of *picric acid*.

Chlorine does not act so energetically on salicin except in the presence of water, when chlorinated salicins are formed, which combine with a certain quantity of water, and we thus have successively



Chromic acid, or a mixture of sulphuric acid and bichromate of potassa, converts salicin into salicylous and formic acids.

§ 1546. Beer-yeast and albuminous substances do not act upon salicin, while synaptase exerts over it a very remarkable power, which should be classed among the phenomena of fermentation, since it decomposes it into glucose, and into a new substance, called *saligenin*  $C_{14}H_8O_4$ , according to the reaction



In order to effect this transformation, 50 parts of powdered salicin, diffused in 200 parts of distilled water, are treated with about 3 parts of synaptase, when the whole is introduced into a bottle, which is well shaken, and heated in a water-bath to  $104^\circ$ . In 10 or 12 hours the transformation is completed, and the greater portion of the saligenin is deposited in the form of small rhombohedral crystals. In order to extract the remainder, the liquid is shaken with its volume of ether, which takes the saligenin from the water, and deposits it on evaporation. Glucose remains in the aqueous solution, and may be easily recognised by its optical properties, or by causing it to ferment with yeast.

Saligenin dissolves in all proportions in boiling water, but it requires 15 parts for solution at the ordinary temperature, and it is very soluble in alcohol and ether, without possessing rotatory power. It melts at  $179.6^\circ$ , while the prolonged action of heat converts it into

saliretin, which transformation is also very rapidly effected by dilute mineral acids. A *mono*, *bi*, and *trichlorinated saligenin* has been obtained by causing synaptase to act on mono, bi, and trichlorinated salicin; which fact is remarkable, because it shows that the substitution of chlorine for hydrogen in salicin does not prevent fermentation.

*Salicylous Acid*  $C_{14}H_5O_3, HO$ .

§ 1547. We have said (§ 1543) that salicylous acid is merely the oil extracted from the flowers of the meadow-sweet, by distillation with water. It does not exist in them ready formed, for the flowers may be exhausted by alcohol without obtaining a trace of it; but it is produced during the distillation of the flowers with water; probably by a phenomenon of fermentation analogous to that producing oil of bitter almonds, when the pulp of the almond is digested with tepid water. The distillation of the flowers of the meadow-sweet with water yields, in addition to salicylous acid, an essential oil, isomeric with oil of turpentine, and a volatile substance which crystallizes. But by shaking the distilled product with caustic potassa, the salicylous acid alone combines with the alkali, and, if the whole be again distilled, the volatile oil and crystalline substance volatilize with the water, while the salicylite of potassa remains in the retort. The salt being decomposed by sulphurous acid, and the distillation recommenced, the salicylous acid, set free, condenses in the receiver.

It is more easy to obtain salicylous acid from salicin by introducing a mixture of 3 parts of the latter substance with 3 parts of bichromate of potassa and 24 parts of water into a retort, and shaking it frequently until complete solution is effected, when  $4\frac{1}{2}$  parts of concentrated sulphuric acid, dissolved in 12 parts of water, are added, and the whole is again shaken. Reaction gradually ensues, and when it appears to be terminated, the temperature is gradually raised, and the distilled products are collected in a well-cooled receiver. The latter are composed of an aqueous solution, slightly acid, containing a small quantity of formic acid, and a reddish oil which collects at the bottom of the aqueous liquid. The oil is decanted and digested for 24 hours over chloride of calcium, and then rectified anew, by which means perfectly pure salicylous acid is obtained.

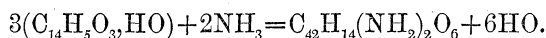
Salicylous acid, or the essential oil of *spiræa ulmaria*, is a colourless liquid, assuming a red tinge on exposure to the air, of an odour similar to that of the oil of bitter almonds, and staining the skin yellow, the stains disappearing as rapidly as those of iodine. It boils at  $384.8^\circ$ , and its density at  $55.4^\circ$  is 1.173, while the density of its vapour is 4.27, and its equivalent  $C_{14}H_5O_3, HO$  is represented by 4 volumes. It has no rotatory power. It is nearly insoluble in water, but dissolves in all proportions in alcohol and ether; and although its solutions do not redden tincture of litmus, they will

decompose the alkaline carbonates, even when cold. It is important to remark that the formula and density of vapour of salicylous acid is the same as that of benzoic acid, furnishing a curious example of isomerism.

Salicylous acid forms two compounds with potassa; and salicylite of potassa  $\text{KO}, \text{C}_{14}\text{H}_5\text{O}_3 + 2\text{HO}$  is obtained as a yellow crystalline mass when salicylous acid is added to a concentrated solution of potassa. By dissolving it in absolute alcohol, the salt is deposited in crystalline lamellæ of a golden yellow colour. By means of this salt, the salicylites of baryta, lime, zinc, lead, mercury, and silver can be prepared by double decomposition. The aqueous solution of salicylite of potassa is readily decomposed, and yields formiate of potassa and a salt of potassa formed by a black substance  $\text{C}_{20}\text{H}_8\text{O}_{10}$ , to which the name of *melanic acid* has been given.

By dissolving salicylate of potassa in hot alcohol, and adding an additional quantity of salicylous acid, the liquid, on cooling, deposits colourless aciculæ of a salt of the formula  $(\text{KO} + \text{HO}), 2\text{C}_{14}\text{H}_5\text{O}_3$ , which may be called *bisalicylite of potassa*, and is more fixed than the neutral salicylite.

Salicylous acid absorbs ammoniacal gas, and is converted into yellow and crystalline *salicylite of ammonia*  $(\text{NH}_3, \text{HO}), \text{C}_{14}\text{H}_5\text{O}_3$ , the same compound being formed when salicylous acid is dissolved in an aqueous solution of ammonia; while, if the acid be first dissolved in 3 times its volume of alcohol, and ammonia be added by drops, yellow aciculæ are formed, which readily dissolve when the temperature is raised. On cooling, the new product is deposited in crystals of a golden yellow colour, with the formula  $\text{C}_{43}\text{H}_{18}\text{N}_2\text{O}_6 = \text{C}_{42}\text{H}_{14}(\text{NH}_2)_2\text{O}_6$ , ensuing from the following reaction:



It has been called *salhydramide*, and is insoluble in water, even at the boiling point.

Salicylous acid absorbs chlorine, even when cold, and the reaction takes place with elevation of temperature, chlorohydric acid being disengaged, and the oil at last becoming solid. By dissolving it in alcohol, crystalline, colourless, and pearly lamellæ are deposited, of *monochlorinated salicylous acid*  $\text{C}_{14}\text{H}_4\text{ClO}_3 + \text{HO}$ , which forms well marked salts, of the general formula  $\text{RO}, \text{C}_{14}\text{H}_4\text{ClO}_3$ , and yields, with ammoniacal gas, *monochlorinated salicylamide*  $\text{C}_{42}\text{H}_{11}\text{Cl}_3(\text{NH}_2)_2\text{O}_6$ .

Bromine forms a *monochlorinated salicylic acid*  $\text{C}_{14}\text{H}_4\text{BrO}_3, \text{HO}$ .

If salicylous acid be heated with nitric acid of medium strength, hyponitric acid is disengaged, and the oil is converted into a crystalline mass, which is purified by dissolving it in boiling water after having washed it with a small quantity of cold water. The solution deposits, by spontaneous evaporation, yellow prismatic crystals of *nitrosalicylous acid*  $\text{C}_{14}\text{H}_4(\text{NO}_4)\text{O}_3, \text{HO}$ , which combines with bases,

and forms salts possessing detonating properties by an elevation of temperature.

*Salicylic Acid*  $C_{14}H_5O_5, HO$ .

§ 1548. When salicylous acid is heated with an excess of hydrate of potassa, hydrogen is disengaged; and if the operation be arrested at the moment of the cessation of the evolution of gas, the mass be dissolved in water, and an excess of chlorohydric acid added, crystals are precipitated, which are purified by recrystallization from boiling water. They are formed by a new acid, *salicylic*  $C_{14}H_5O_5, HO$ , which arises from the following reaction:



This acid results from the simple combination of 1 equivalent of salicylous acid with 2 equivalents of oxygen.

Salicylic acid dissolves in boiling water, but is nearly insoluble in cold water: it dissolves freely in alcohol and ether; volatilizes without change, and then produces crystals resembling those of benzoic acid: it reddens litmus and decomposes the carbonates. It has no action on polarized light. Bromine and chlorine act on it readily, and produce mono and bibrominated, mono and bichlorinated salicylic acids.

Treated with fuming nitric acid, salicylic acid is converted into a reddish resinoid mass, which is to be washed with cold and dissolved in boiling water: yellowish, fusible, and volatile aciculæ, of *nitro-salicylic acid*  $C_{14}H_4(NO_4)O_5, HO$  are deposited from the solution.

*Methylosalicylic Ether*  $C_2H_3O, C_{14}H_5O_5$ .

§ 1549. By distilling a mixture of 2 parts of methylic alcohol, 2 parts of salicylic acid, and 1 part of sulphuric acid, this compound ether is readily obtained, as a colourless or slightly yellowish liquid, boiling at  $428^\circ$ , and of the density 1.18 at  $50^\circ$ , the density of its vapour being 5.42, and its equivalent  $C_2H_3O, C_{14}H_5O_5$  corresponding to 2 volumes of vapour. It is nearly insoluble in water, but dissolves readily in alcohol and ether.

Methylosalicylic ether exists ready formed in a native essential oil, called *wintergreen*, and obtained from the *gaultheria procumbens*. The oil of gaultheria comes principally from New Jersey, where the plant grows in great abundance. By distilling the oil, there is disengaged, first a carburetted hydrogen isomeric with oil of terpenite, and subsequently methylosalicylic ether.\*

Methylosalicylic ether is a true acid, which combines with potassa, forming a salt which crystallizes in pearly spangles. But if an excess of potassa be used, particularly when assisted by heat, the

\* The interesting discovery of the artificial formation of this substance, by Cahours, was first indicated by W. Proctor, of Philadelphia, who first proved that the oil of gaultheria belonged to the salicylic series.—*J. C. B.*

ether undergoes the ordinary decomposition of compound ethers, and is converted into alcohol and salicylic acid.

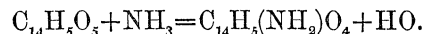
Chlorine and bromine readily act on methylosalicylic ether, and yield chlorinated and brominated products :

Monochlorinated methylosalicylic ether.....	$C_2H_3O, C_{14}H_4ClO_5,$
Bichlorinated	“ “ ..... $C_2H_3O, C_{14}H_3Cl_2O_5,$
Monobrominated	“ “ ..... $C_2H_3O, C_{14}H_4BrO_5,$
Bibrominated	“ “ ..... $C_2H_3O, C_{14}H_3Br_2O_5.$

With a hot solution of potassa, these substances are decomposed into methylic alcohol and mono or bichlorinated or brominated salicylic acid.

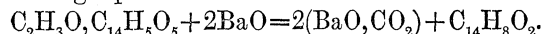
Fuming nitric acid converts methylosalicylic ether into *nitromethylosalicylic ether*  $C_2H_3O, C_{14}H_4(NO_4)O_5.$

By introducing into a well-corked bottle 1 volume of methylosalicylic ether, and 5 or 6 volumes of a concentrated solution of ammonia, the ether disappears after some time, and by then evaporating the liquid and distilling the residue, a yellow mass is obtained, which may be converted into crystalline aciculæ, by solution in boiling water. The formula of this substance is  $C_{14}H_5(NH_2)O_4,$  and it is generated from anhydrous salicylic acid, according to the following equation :



This substance, which has been called *salicylamide*, is soluble in boiling water, but nearly insoluble in cold water, and dissolves readily in alcohol and ether. It volatilizes without alteration, and with acids regenerates ammonia and salicylic acid. By causing ammonia, under similar circumstances, to act on chlorinated, brominated, or nitric products, derived from methylosalicylic ether, *mono* and *bichlorinated*, *mono* and *bibrominated*, and *nitric salicylamides* are obtained.

Lastly, by allowing methylosalicylic ether to fall on anhydrous lime or baryta, carbonates of these bases, and a new substance  $C_{14}H_5O_2,$  called *anisole*, are formed, the reaction being expressed by the following equation :



Anisole is a colourless, very fluid liquid, of an agreeable aromatic odour, boiling at  $302^\circ$ , insoluble in water, but very soluble in alcohol and ether.

#### *Vinosalicylic Ether* $C_4H_5O, C_{14}H_5O_5.$

§ 1550. By distilling a mixture of 2 parts of absolute alcohol,  $1\frac{1}{2}$  part of salicylic acid, and 1 part of sulphuric acid, we obtain *vinosalicylic ether*, which, like its analogue of the methylic series, combines with bases. It also forms salicylamide with ammonia, and produces, with chlorine, bromine, and nitric acid, chlorinated, bro-

minated, and nitric ethers, corresponding to those formed by methylosalicylic ether.

#### OIL OF CINNAMON AND THE CINNAMIC SERIES.

§ 1551. Oil of cinnamon is found in commerce, being imported from Ceylon and China. That from China is more esteemed, because it has an agreeable smell, peculiar to cinnamon-bark, while the Ceylon oil has a mixed smell of cinnamon and bed-bugs, and its composition appears to be more complicated. By digesting powdered cinnamon-bark with water for 12 hours, and then saturating the water with sea-salt, and subjecting the whole to distillation, a milky water passes over, which deposits an essential oil, of a more or less reddish yellow, and resembling the cinnamon-oils of commerce.

Oils of cinnamon appear to be mixtures of an essential oil, to which the name of *hydruret of cinnamyl* has been given, and which we shall consider as the oil of cinnamon, properly so called, with other oils which have not yet been studied. The oil of cinnamon, properly so called, is separated by agitating the oil of cinnamon of commerce with concentrated nitric acid, when, in a few hours, long prismatic crystals are formed, which are separated and pressed between folds of tissue-paper. Water readily decomposes them, and yields an essential oil  $C_{18}H_8O_2$ , which is regarded as pure oil of cinnamon; the water then containing nitric acid. The crystals, which may be considered as a nitrate of the oil of cinnamon, present the formula  $C_{18}H_8O_2 \cdot NO_5 + HO$ .

Pure oil of cinnamon is a colourless, oleaginous liquid, which becomes perfectly solid with nitric acid, and reproduces the crystalline compound just mentioned. It absorbs chlorohydric acid gas, and forms a compound  $C_{18}H_8O_2 \cdot HCl$ . Chlorine acts powerfully upon it, and, if its action be exhausted by heat, and the product distilled in a current of chlorine, we obtain white acicular crystals of *quadri-chlorinated oil of cinnamon*  $C_{18}H_4Cl_4O_2$ , called also *chlorocinnose*.

Oil of cinnamon absorbs the oxygen of the air, and is converted into a peculiar substance  $C_{18}H_7O_3 \cdot HO$ , called *cinnamic acid*, which may be regarded as being derived from the oil  $C_{18}H_8O_2$ , by the substitution of 1 equivalent of oxygen for one of hydrogen.\* The acid is also formed when oil of cinnamon is treated with hydrate of potassa, hydrogen being disengaged; while, if the action of the potassa be prolonged, benzoate of potassa  $KO \cdot C_{14}H_5O_3$  only is found in the liquid.

Concentrated boiling nitric acid converts oil of cinnamon into oil of bitter almonds and into nitrobenzoic acid.

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\* This view is certainly incorrect, because oxygen will not replace hydrogen. The oil of cinnamon simply gains 2 equivalents of oxygen, while 1 equivalent of water parts from it and becomes basic.—*W. L. F.*

*Cinnamic Acid*  $C_{18}H_7O_3.HO$ .

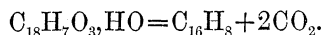
§ 1552. We have said that cinnamic acid is formed by the oxidation of oil of cinnamon; but it exists already formed in balsams of Tolu and Peru, from which it is generally extracted by running the the balsam of Peru into milk of lime, which is constantly stirred, when the resins of the balsam combine with the lime and produce insoluble compounds. By treating the whole with boiling water, the cinnamate of lime only is dissolved, and crystallizes on the cooling of the liquid; and by decomposing a boiling solution of cinnamate of lime with chlorohydric acid, the cinnamic acid is deposited, on cooling, in the form of pearly, colourless lamellæ, which melt at  $264.2^\circ$ , and boil at about  $570^\circ$ . The alkaline and alkalino-earthly cinnamates, are soluble in water, while the majority of the other metallic cinnamates are insoluble; and their general formula is  $RO.C_{18}H_7O_3$ , when they contain no water of crystallization.

By causing chlorohydric acid gas to act on cinnamic acid dissolved in absolute alcohol or in anhydrous wood-spirit, cinnamic ethers  $C_4H_5O.C_{18}H_7O_3$  and  $C_2H_3O.C_{18}H_7O_3$  are obtained.

By heating 1 part of cinnamic with 8 parts of concentrated nitric acid, a spongy mass results, which is to be washed with water, and afterward dissolved in boiling alcohol. The alcoholic liquid deposits, on cooling, acicular crystals, fusible at a high temperature, of nitrocinnamic acid  $C_{18}H_6(NO_4)O_3.HO$ .

*Cinnamen*  $C_{16}H_8$ .

§ 1553. When vapours of cinnamic acid are passed through a glass tube heated to a dull-red, carbonic acid is disengaged, with a carburetted hydrogen, cinnamen  $C_{16}H_8$ , which condenses in the form of a colourless liquid:



The same substance is obtained by decomposing cinnamate of copper by heat, or subjecting to dry distillation certain resins, particularly *storax*, a kind of balsam found in commerce. The best method of preparing cinnamen consists in mixing 10 kilog. of storax with  $3\frac{1}{2}$  kilog. of carbonate of soda, and distilling the whole in an alembic with a sufficient quantity of water, when a milky water passes over, which by resting, parts with the cinnamen, which floats on its surface. Storax thus yields rather more than  $\frac{1}{100}$  of its weight of cinnamen; and the oil obtained is left for some time on chloride of calcium, and then distilled.

Cinnamen is a colourless liquid, of a penetrating odour, of the density 0.95 at  $32^\circ$ , and boiling at  $294.8^\circ$ . When heated to  $390^\circ$  in a glass tube hermetically closed, it is converted into an isomeric substance, *metacinnamen*, which is solid, and insoluble in water, al-



cohol, and ether. Heated to distillation, metacinnamen again passes into the state of cinnamen.

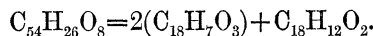
Chlorine, when cold, reacts upon cinnamen, and converts it into a viscous fluid, of the formula  $C_{16}H_8Cl_2$ , but which we shall write  $C_{16}H_7Cl, HCl$ . Distilled over quicklime, or treated with an alcoholic solution of potassa, this compound yields *monochlorinated cinnamen*  $C_{16}H_7Cl$ . Monobrominated cinnamen  $C_{16}H_7Br$  is also obtained, as well as its bromohydrate  $C_{16}H_7Br, HBr$ .

#### *Balsams of Peru.*

§ 1554. Two species of balsam of Peru are found in commerce: a liquid balsam, which alone has been properly studied; and a solid and nearly black balsam, which appears to be a modification of the first. Balsam of Peru is dissolved in alcohol at  $96.8^\circ$ , and an alcoholic solution of potassa added, when the resin contained in the balsam combines with the potassa, with which it forms a compound nearly insoluble in water, while the cinnamate of potassa remains in solution. By diluting the alcoholic liquid with water, the cinnamate of potassa remains in solution, while a complex oil separates, retaining a small quantity of resin. This is treated with oil of naphtha, which leaves the resin, and dissolves the oil; and the latter is cooled in a refrigerating mixture, and treated with weak alcohol, equally cold. An oily portion, which is *cinnameïn*, is thus extracted, and the residue is dissolved in boiling alcohol, which deposits a crystalline substance, *metacinnameïn*.

Metacinnameïn is a solid, very fusible substance, insoluble in water, but readily soluble in alcohol and ether, isomeric with oil of cinnamon, and being changed by hydrate of potassa into cinnamic acid, with disengagement of hydrogen.

Cinnameïn is a liquid, which does not volatilize without change; and a concentrated solution of potassa decomposes it, by prolonged contact, into cinnamic acid and a new oily liquid, lighter than water, called *peruvïn*  $C_{18}H_{12}O_2$ . The composition of cinnameïn corresponds to the formula  $C_{54}H_{26}O_8$ , and it may be represented by 2 equivalents of anhydrous cinnamic acid, and 1 equivalent of peruvïn, according to the equation



Balsam of Peru may therefore be considered as formed of cinnameïn, metacinnameïn, cinnamic acid, and resinous substances.

#### *Balsam of Tolu.*

§ 1555. Balsam of Tolu is composed of resin, cinnamic acid, and a carburetted hydrogen, isomeric with oil of turpentine, and called *tolen*. This balsam, heated with a solution of caustic potassa, yields benzoic acid, which is probably formed at the expense of the resin. Tolen is a colourless liquid, boiling at about  $320^\circ$ .

COUMARIN  $C_{18}H_8O_4$ .

§ 1556. The name of *coumarin* has been given to a crystalline odoriferous substance extracted from the Tonka bean, but which appears to exist in the flowers of several plants: thus, its existence has been detected in the flowers of the melilot, and the sweet woodruff, called *waldmeister* by the Germans, who use it in the preparation of an agreeable beverage, called *maitrank*. Coumarin is prepared by digesting bruised Tonka beans with alcohol at  $96.8^\circ$ , when the alcoholic liquor, subjected to distillation, yields a syrupy residue, which, on cooling, sets into a crystalline mass. This is dissolved in boiling water, and the liquid being discoloured by animal black, the coumarin separates in white crystalline aciculæ during the cooling.

Coumarin melts at  $122^\circ$ , and boils at  $518^\circ$ , without any change, and its smell is agreeably aromatic, while its vapours exert a powerful action on the brain. It dissolves freely in boiling water, but is almost wholly deposited from it on cooling. It dissolves in cold monohydrated nitric acid, with evolution of heat; and if the liquid be then diluted with water, a cheesy precipitate is formed, which dissolves in boiling alcohol, and separates again, on cooling, in small crystalline aciculæ. It is *nitrocoumarin*  $C_{18}H_5(NO_4)O_4$ , melting at  $338^\circ$ , and then subliming without alteration in white and pearly crystals. If the action of the nitric acid be prolonged, the coumarin is converted into *trinitrophenic acid*  $C_{12}H_2(NO_4)_3HO$ , which shall hereafter be described.

Coumarin dissolves in a weak solution of potassa, and is precipitated from it without change when the alkali is saturated with an acid; while, if the solution is concentrated, and it be boiled, adding some pieces of hydrate of potassa, *coumaric acid*  $C_{18}H_7O_5HO$  is formed; and if the temperature be greatly raised, hydrogen is disengaged and salicylic acid formed at the same time. The alkaline substance, treated with water, and then supersaturated with chlorohydric acid, deposits coumaric acid, which is washed with cold water, to dissolve the salicylic acid which may have been precipitated with it, and then dissolved in ammonia, which leaves the coumarine unchanged. The ammoniacal liquid is boiled to drive off the excess of ammonia, when nitrate of silver is added, effecting a precipitate of coumarate of silver, which, with chlorohydric acid, yields free coumaric acid, removable by means of ether.

Coumaric acid is a white crystalline substance, very soluble in alcohol and ether, dissolving freely in boiling, but nearly insoluble in cold water, and melting at about  $374^\circ$ . The general formula of the coumarates is  $RO, C_{18}H_7O_5$ , from which it will be seen that anhydrous coumaric acid only differs from coumarin by the addition of 1 equivalent of water.

VOL. II.—3 F

## OIL OF ANISEED, AND THE ANISIC SERIES.

§ 1557. By distilling aniseed with water, a slightly yellowish essential oil is obtained, possessing the characteristic odour of the seed, and which, at a low temperature, consolidates almost wholly into a crystalline mass. This mass is pressed between tissue-paper, when a liquid portion, of which the nature is not yet known, separates; and it is redissolved in alcohol, which deposits, on evaporation, white crystalline lamellæ, fusible at  $64.4^{\circ}$ , and boiling at about  $428^{\circ}$ . This substance is called *concrete oil of aniseed*, and its formula is  $C_{20}H_{12}O_2$ . When made liquid by heat, it rotates to the left.

Oil of aniseed absorbs chlorohydric gas and forms a compound  $C_{20}H_{12}O_2, 2HCl$ ; while chlorine acts upon it and produces compounds derived by substitution: thus,

A trichlorinated oil.....  $C_{20}H_9Cl_3O_2$

And a quadrichlorinated oil.....  $C_{20}H_8Cl_4O_2$

have been separated.

With bromine, a tribrominated oil  $C_{20}H_9Br_3O_2$ , and, with nitric acid, the binitric oil  $C_{20}H_{10}(NO_4)_2O_2$ , have been obtained.

When oil of aniseed is heated with dilute nitric acid, a reddish oil falls to the bottom of the acid liquid, by distilling which, after having washed it with water, two substances are collected; one being crystalline, and a new acid, called *anisic*  $C_{16}H_7O_5, HO$ ; and the other liquid, and consisting of a neutral substance  $C_{16}H_8O_4$ , to which the name of *hydruret of anisyle* has been given. It will be seen that anisic acid may be considered as resulting from the substitution of 1 equiv. of oxygen for 1 equiv. of hydrogen,\* in the molecule of hydruret of anisyl, and there exists, therefore, between these two substances, the same relation as between oil of bitter almonds  $C_{14}H_6O_2$  and benzoic acid  $C_{14}H_5O_3, HO$ .

The mixture of the two substances is treated with a weak solution of potassa, which dissolves the anisic acid, when the hydruret of anisyl is distilled in a current of carbonic acid gas.

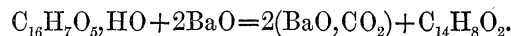
Hydruret of anisyl is a colourless gas, which absorbs the oxygen of the air, and is converted into anisic acid. Chlorine acts upon it and yields a monochlorinated product  $C_{16}H_7ClO_4$ . When hydruret anisyl is dropped on melted caustic potassa, hydrogen is disengaged and anisic acid formed.

Anisic acid crystallizes in white inodorous needles, which melt at  $347^{\circ}$ , and volatilize without change, and it dissolves readily in boiling water, alcohol, and ether. The general formula of its salts is  $RO, C_{16}H_7O_5$ .

Chlorine and bromine form chlorinated and brominated anisic acids, while nitric acid forms first a *nitranisic acid*  $C_{16}H_6(NO_4)O_5, HO$ .

\* The hydruret of anisyl takes up 2 equiv. of oxygen and loses 1 equiv. of water, which becomes basic with the acid formed.—*W. L. F.*

and then, if a mixture of fuming nitric and concentrated sulphuric acid be made to act upon it, it forms *trinitranisic acid*  $C_{16}H_4(NO_4)_3O_5, HO$ . Anisic acid yields *anisole*  $C_{14}H_8O_2$  by distillation with caustic baryta:



*Anisen or Benzoen*  $C_{14}H_8$ .

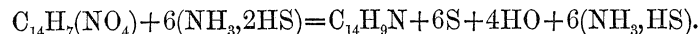
§ 1558. These names have been given to a carburetted hydrogen  $C_{14}H_8$ , which is to anisic acid  $C_{16}H_7O_5, HO$  what benzin  $C_{12}H_6$  is to benzoic acid  $C_{14}H_5O_3, HO$ . It is prepared by distilling the resin of balsam of tolu, and collecting the oil, which is again distilled at a temperature not exceeding  $284^\circ$ ; the distilled portion being rectified several times over caustic potassa, and dried over chloride of calcium. It is a very fluid, colourless liquid, boiling at  $226.4^\circ$ , and its density is 0.87 at  $64.4^\circ$ ; while that of its vapour is 3.26, its equivalent  $C_{14}H_8$  corresponding therefore to 4 volumes of vapour.

Chlorine acts readily upon anisen, and yields

Monochlorinated anisen.....	$C_{14}H_7Cl$ ,
Trichlorinated “ .....	$C_{14}H_5Cl_3$ ,
Sesquichlorinated “ .....	$C_{14}H_2Cl_6$ ,

as well as the following compounds, which these substances form with chlorohydric acid:  $C_{14}H_5Cl_3, HCl$ ,  $C_{14}H_5Cl_3, 2HCl$ ,  $C_{14}H_5Cl_3, 3HCl$ .

§ 1559. Nitric acid produces *nitranisen*  $C_{14}H_7(NO_4)$  and *binitranisen*  $C_{14}H_6(NO_4)_2$ . Nitranisen yields, with sulphhydrate of ammonia, an alkaloid  $C_{14}H_9N$  which is called *toluidin*; the reaction being analogous to that which forms anilin with nitrobenzin, (§ 1538,) according to the equation



Nitranisen must be dissolved in alcohol, and ammonia and sulphydric gas be successively passed through the liquid, which, after being left for some days to itself, and then gently heated, is again subjected to the successive action of ammoniacal and sulphydric gas, and is finally saturated with chlorohydric acid, and evaporated to one-third, when the residue is distilled with caustic potassa. The toluidin condenses in the receiver in the form of a colourless oil, which, on cooling, sets into a crystalline mass. In order to purify it, oxalic acid is added, and it is treated with alcohol, which dissolves the oxalate of toluidin, and leaves the oxalate of ammonia. Oxalate of toluidin is decomposed by caustic potassa, and the isolated toluidin coagulates in a crystalline crust on the surface of the liquid.

Toluidin melts at  $104^\circ$ , and boils at about  $390^\circ$ , and its salts crystallize readily; their general formula being  $(C_{14}H_9N, HO)\bar{A}$ .

## OIL OF CUMIN AND THE CUMINIC SERIES.

§ 1560. Cumin seed,\* distilled with water, yields an essential oil composed of carburetted hydrogen  $C_{20}H_{14}$ , *cymen*, and another volatile oil  $C_{20}H_{12}O_2$ , called *cuminole*. When oil of cumin is again distilled, the cymen passes over first, at about  $392^\circ$ , which temperature is maintained so long as any thing passes over, when the receiver is changed and the temperature raised by passing a current of carbonic acid gas through the retort: the cuminole then distils.

Cuminole is a colourless liquid, having the smell of cumin, and an acrid and burning taste, and it boils at  $428^\circ$ ; the density of its vapour being 5.24, and its equivalent  $C_{20}H_{12}O_2$  being represented by 4 volumes of vapour. It rapidly absorbs the oxygen of the air, and is converted into *cuminic acid*  $C_{20}H_{11}O_3.HO$ , which transformation it readily undergoes when boiled with a concentrated solution of potassa, or when dropped into melted hydrate of potassa; hydrogen being disengaged in the latter case. Oxidizing reagents, such as nitric acid, chlorine in the presence of water, chromic acid, etc., also convert cuminole into cuminic acid.

Chlorine acts on cuminole when exposed to diffused light, and produces *monochlorinated cuminole*  $C_{20}H_{11}ClO_2$ ; while bromine forms monobrominated cuminole  $C_{20}H_{11}BrO_2$ .

*Cuminic Acid*  $C_{20}H_{11}O_3.HO$ .

§ 1561. This acid is generally prepared by melting hydrate of potassa in a retort having a pointed tube fitted to its tubulure, through which the crude oil of cumin drops; when the cymen is not acted on, and distils without change, while the cuminole is decomposed by contact with the alkali, being converted into cuminic acid, which remains combined with the potassa. The alkaline mass being dissolved in water, and heated to ebullition, an excess of chlorohydric acid is added, which precipitates the cuminic acid in flakes; and the latter, redissolved in alcohol, are transformed into beautiful prismatic tablets.

Cuminic acid melts at a few degrees above  $212^\circ$ , and boils at about  $500^\circ$ , subliming without alteration in crystalline aciculæ. Hot water dissolves it slightly, and deposits it entirely on cooling, while it dissolves freely in alcohol and ether. The general formula of the cumينات is

*Cymen*  $C_{20}H_{14}$ .

§ 1562. We have described (§ 1560) the best method of separating cymen from crude oil of cumin. It is a colourless liquid, of an agreeable odour, resembling that of lemon; it boils at  $347^\circ$ , and

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\* The seed of *cuminum cyminum*.—W. L. F.

the density of its vapour is 4.64, its equivalent being represented by 4 volumes of vapour. Nordhausen sulphuric acid dissolves it, and produces a compound acid  $C_{20}H_{13}S_2O_5HO$  which forms a soluble salt with baryta.

#### ESSENTIAL OIL OF CLOVES, AND THE EUGENIC SERIES.

§ 1563. Cloves and Jamaica pimento yield, by distillation with water, a yellowish essential oil of a complicated character, for four distinct substances have already been separated from it: a carburuetted hydrogen, isomeric with oil of turpentine; an oxygenated essential oil  $C_{20}H_{11}O_3HO$ , called *eugenic acid*, because it possesses acid properties; and two neutral crystalline substances, *eugenin* and *cariophyllin*.

Water which has been distilled over cloves gradually deposits a substance crystallized in pearly spangles, consisting of eugenin  $C_{20}H_{12}O_4$ , isomeric with eugenic acid.

Crude oil of cloves deposits, after some time, fine colourless aciculæ of caryophyllin  $C_{20}H_{16}O_2$ , isomeric with the camphor from the family of the laurels.

If crude oil of cloves be mixed with a concentrated solution of potassa, a crystalline mass, of the consistence of butter, is formed, which is separated and distilled with water, when the oil, isomeric with turpentine alone, passes over, while the eugenic acid remains in the residue in the state of eugenate of potassa. The residue is treated with chlorohydric acid, which separates the eugenic acid from it in the form of a colourless, oleaginous liquid, boiling at  $473^\circ$ , which is distilled in a current of carbonic acid gas.

Eugenic acid absorbs the oxygen of the air, and is converted into a resinous substance. It forms crystallizable salts with potassa, soda, and lime, of the general formula  $RO, C_{20}H_{11}O_3$ .

#### OIL OF POTATO-SPIRIT,\* OR AMYLIC ALCOHOL $C_{10}H_{12}O_2$ .

§ 1564. This oil is obtained when, in the manufacture of alcohol, the liquors resulting from the action of ferment on the fecula of the potato are distilled; and it is also formed in the distillation of certain alcoholic products obtained in the fermentation of the cerealia or of grapes; the oil, therefore, constantly accompanying the products of alcoholic fermentation. Toward the close of the distillation of brandy from fecula, the largest proportion of the oil is obtained, when a milky water passes over, on the surface of which, after resting for some time, the oil floats. The composition of this oil is very complicated, and when distilled, it begins to boil at about  $185^\circ$ , while its boiling point rises to  $269.6^\circ$ , at which it remains for some time; the last product, which is collected separately, being almost wholly composed of the essential oil required. It is purified by several rectifications, and the oil which boils exactly at  $269.6^\circ$  should alone be regarded as pure.

\* Also called *fousel oil*.—W. L. F.

Oil of potato-spirit is an oily, colourless liquid, of a strong and disagreeable odour and an acrid and burning taste. Its density at  $59^{\circ}$  is 0.818, while that of its vapour is 3.15, its equivalent  $C_{10}H_{12}O_2$  corresponding to 4 volumes. At  $-4.0^{\circ}$  it solidifies in crystalline leaflets; and it stains paper like the essential oils, but the spot quickly disappears, because the oil volatilizes. Oil of potato-spirit does not ignite at the approach of a burning substance, unless it be at a temperature of  $120^{\circ}$  or  $140^{\circ}$ , its vapour supporting combustion only at that degree. It is not sensibly soluble in water, but dissolves in all proportions in alcohol and ether. Oil of potato-spirit rotates toward the left.

A large number of compounds is derived from the oil, so analogous to those obtained by means of alcohol and wood-spirit, that chemists have not hesitated to regard this oil as a true alcohol, to which they have given the name of *amylic alcohol*. In our subsequent investigation of these compounds, we shall follow the same order as in those of the vinic and methylic compounds, since their analogy will be thus more easily understood.

#### *Action of Sulphuric Acid on Amylic Alcohol.*

§ 1565. By shaking together equal parts of oil of potato-spirit and concentrated sulphuric acid, a brown liquor is formed, which, when saturated with carbonate of baryta, yields sulphate of baryta and a soluble salt of baryta, the solution of which is bleached by animal black. The liquor, when evaporated at a gentle heat, yields small crystalline lamellæ of *sulphamylate of baryta*, of the formula  $BaO, (C_{10}H_{11}O, 2SO_3) + 3HO$ , which is decomposed at the boiling point. Its solution, when decomposed by sulphate of potassa, yields, after evaporation and dessication in vacuo, a crystalline residue of *sulphamylate of potassa*  $KO, (C_{10}H_{11}O, 2SO_3)$ . If, on the contrary, the baryta be precipitated by sulphuric acid added dropwise, a solution of free sulphamylic acid is obtained, which, boiling readily, decomposes into sulphuric acid and amylic alcohol  $C_{10}H_{12}O_2$  or  $C_{10}H_{11}O, HO$ .

§ 1566. If an excess of concentrated sulphuric acid be made to act on amylic alcohol, and it be heated to boiling, we obtain a carburetted hydrogen  $C_{10}H_{10}$ , called *amylen*, which is to amylic alcohol  $C_{10}H_{11}O, HO$  what olefiant gas  $C_4H_4$  is to vinic alcohol  $C_4H_5O, HO$ . All reagents which abstract water from vinic alcohol modify amylic alcohol in an analogous manner: thus both concentrated and anhydrous phosphoric acid, fluoboric and fluosilicic gases, and chloride of zinc produce the same effect as concentrated sulphuric acid. As the chloride of zinc effects the neatest decomposition, it is generally used in the preparation of pure amylen. Amylic alcohol is heated in a retort, with a solution of chloride of zinc marking  $70^{\circ}$  on the hydrometer, the retort being frequently shaken while the temperature rises: when the oil is finally wholly dissolved, distillation

may be begun. The liquid, when distilled, is again rectified in a tubulated retort furnished with a thermometer, and only the most volatile part is collected.

Amylen thus obtained is a colourless, very fluid liquid, boiling at  $102.2^{\circ}$ , and the density of its vapour being 2.45, its equivalent  $C_{10}H_{10}$  corresponds to 4 volumes of vapour, like that of olefant gas.

Amylen can form two isomeric products: *paramylen*  $C_{20}H_{20}$ ; and *metamylen*, of which the formula is  $C_{30}H_{30}$  or  $C_{40}H_{40}$ . These two products generally arise at the same time as the amylen, and are found in the last products of distillation; but they may be obtained directly by distilling amylen with chloride of zinc several times successively. Paramylen boils at about  $320^{\circ}$ , and the density of its vapour is double that of amylen; for which reason its formula has been written  $C_{20}H_{20}$ . Metamylen distils only at  $570^{\circ}$ ; but it probably has not yet been obtained in a state of purity.

§ 1567. *Amylic ether*  $C_{10}H_{11}O$  has not yet been prepared by the action of sulphuric acid on amylic alcohol; but it has been obtained by causing an alcoholic solution of potassa to act on amylochlorohydric ether  $C_{10}H_{11}Cl$ , of which we shall speak presently. It is a colourless liquid, of an agreeable odour, and boiling at  $230^{\circ}$ .

*Compound Amylic Ethers, and Compound Amylic Acids.*

§ 1568. As yet we are acquainted neither with *amylosulphuric ether*  $C_{10}H_{11}O, SO_3$ , nor with *amylonitric ether*  $C_{10}H_{11}O, NO_5$ ; while an *amylonitrous ether*  $C_{10}H_{11}O, NO_3$  is produced by collecting in amylic alcohol the nitrous vapours which are disengaged when starch is treated with nitric acid. By distillation, the amylonitrous ether separates in the form of a pale, yellow liquid, which is to be washed several times with water, and then with a weak solution of potassa; after which it is dried over chloride of calcium and redistilled. It boils at  $204.8^{\circ}$ , and the density of its vapour is 4.03, so that its equivalent  $C_{10}H_{11}O, NO_3$  corresponds to 4 volumes of vapour, like the corresponding product of the vinic series. The same ether is formed when nitric acid is made to act on amylic alcohol; but it is then mixed with various products of oxidation, particularly with valerianic acid and methylic aldehyde.

By causing boracic acid, melted and reduced to an impalpable powder, to act on amylic alcohol, exactly under the circumstances which have been described for alcohol, (§ 1248,) there remains a residue of *amylobiboracic ether*  $C_{10}H_{11}O, 2BO_3$ , solid at a low temperature, but assuming at about  $248^{\circ}$  a viscous consistence resembling that of fused glass. This substance resists a temperature of  $570^{\circ}$  without decomposition, burns with a green flame, and is decomposed by water.

If chloride of boron be made to act on amylic alcohol, an oily liquid is obtained, which boils without change at about  $527^{\circ}$ , and



consists of *triamylboracic ether*  $3C_{10}H_{11}O,BO_3$ . The density of its vapour is 10.55.

By dropping amylic alcohol into chloride of silicium, shaking the mixture frequently, then distilling it and collecting only the product which passes over at from  $608^\circ$  to  $640^\circ$ , a liquid is obtained, which is to be purified by several distillations, and which consists of *triamylosilicic ether*  $3C_{10}H_{11}O,SiO_3$ . Water decomposes it slowly.

*Amylacetic ether*  $3C_{10}H_{11}O,C_4H_3O_3$  is obtained by distilling 1 part of amylic alcohol, 2 parts of acetate of potassa, and 1 part of concentrated sulphuric acid, the product being washed with an alkaline solution, dried over chloride of calcium, and rectified a last time over litharge. It is a colourless, limpid liquid, of an aromatic odour,\* boiling at  $257^\circ$ , and the density of its vapour being 4.46, its equivalent corresponds to 4 volumes of vapour, like the corresponding ethers of the vinic and methylic series.

Oxalic acid forms two compounds with amylic alcohol, corresponding to those which it produces with vinic and methylic alcohols. When amylic alcohol is heated with oxalic acid, a liquor is obtained, which, when saturated with carbonate of lime, yields a soluble salt of lime, the *amyloxalate of lime*, of which the formula of the crystals is  $CaO,(C_{10}H_{11}O,2C_2O_3)+2HO$ ; and a great number of other amyloxalates may be obtained by double decomposition, by means of this salt.

If, on the contrary, the mixture of amylic alcohol and oxalic acid be distilled, a liquid is obtained, boiling at  $500^\circ$ , and called *amyloxalic ether*  $C_{10}H_{11}O,C_2O_3$ , which rotates toward the right, in an opposite direction to that of amylic alcohol. This liquid, treated with an aqueous solution of ammonia, yields oxamide; while if ammoniacal gas be passed through a solution of amyloxalic ether in absolute alcohol, a liquid is obtained which deposits, on evaporation, crystals of *amyloxamic ether*  $C_{10}H_{11}O,(C_4O_5NH_2)$ .

#### *Simple Ethers of the Amylic Series.*

§ 1569. We have described (§ 1567) the mode of preparing simple amylic ether  $C_{10}H_{11}O$ . *Amylochlorohydric ether*  $C_{10}H_{11}Cl$  is obtained by distilling equal parts of perchloride of phosphorus and amylic alcohol, when the product is washed with alkaline water and dried over chloride of calcium. The same substance is also obtained by causing chlorohydric acid to act, for a long time, on the same alcohol; the liquid separating into 3 layers, of which the upper one contains the amylochlorohydric ether. It is a colourless liquid, of an aromatic odour, boiling at  $215.6^\circ$ , and its equivalent corresponds to 4 volumes. Chlorine acts on it, and when its action is exhausted,

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\* The odour of amylacetic ether closely resembles that of the banana, and it is with this substance that the favourite acidulated banana-drops are flavoured.—*W. L. F.*

by exposure to the rays of the sun, a chlorinated product, of the formula  $C_{10}H_3Cl_9$ , is obtained.

By causing 15 parts of amylic alcohol, 8 parts of iodine, and 1 of phosphorus to react at a gentle heat, and then distilling the mixture, we obtain a liquid, which is to be purified by several washings, drying over chloride of calcium, and redistillation. It is *amyliodohydric ether*  $C_{10}H_{11}I$ .

By distilling a concentrated solution of sulphamylate of lime and cyanide of potassium, *amylocyanohydric ether*  $C_{10}H_{11}Cy$  is obtained; and chlorohydrate of amylen heated with an alcoholic solution of monosulphide of potassium produces *amylosulphhydric ether*  $C_{10}H_{11}S$ , a colourless liquid, of a very disagreeable odour, and boiling at  $402.8^\circ$ . Its equivalent is represented by 2 volumes of vapour.

*Sulphamylic alcohol* or *amylic mercaptan*  $C_{10}H_{11}S, HS$  is obtained by distilling amylochlorohydric ether  $C_{10}H_{11}Cl$  with an alcoholic solution of sulphhydrate of sulphide of potassium. It is an oleaginous, colourless liquid, of an alliaceous smell; and it boils at  $242.6^\circ$ , while its density at  $69.8^\circ$  is 0.825. In contact with oxide of mercury it yields *sulphamylomercuric alcohol*  $C_{10}H_{11}S, Hg_2S$ .

#### *Products of the Oxidation of Amylic Alcohol.*

§ 1570. When amylic alcohol is subjected to oxidizing agencies, it is converted into an acid  $C_{10}H_9O_3, HO$ , called *amylic*, identical with an acid extract of the valerian root, and called *valerianic acid*. This acid is to amylic alcohol  $C_{10}H_{11}O, HO$  what acetic acid  $C_4H_3O_3, HO$  is to vinic alcohol  $C_4H_5O, HO$ , and what formic acid  $C_2H_3O_3, HO$  is to methylic alcohol  $C_2H_3O, HO$ . An intermediate product, amylic aldehyde  $C_{10}H_{10}O_2$ , corresponding to the aldehyde of the vinic series, has also been obtained, but it is difficult to isolate it among the products of oxidation of amylic alcohol.

By heating oil of potato-spirit with a mixture of sulphuric acid and bichromate of potassa, there pass over in distillation valerianic acid  $C_{10}H_9O_3, HO$  and amylovalerianic ether  $C_{10}H_{11}O, C_{10}H_9O_3$ . If it be treated by a solution of potassa, the valerianic acid is dissolved in the state of valerianate of potassa, while the amylovalerianic ether remains, which in its turn may be wholly transformed into valerianic acid, if its vapours be passed over sodic lime. The oil of valerian is, in fact, converted into valerianic acid, when its vapours are passed over sodic lime placed in a flask heated in an oil-bath to a temperature between  $400^\circ$  and  $480^\circ$ ; hydrogen only being disengaged in the beginning, while toward the close of the operation this gas is accompanied by carburetted hydrogens. The flask is allowed to cool, and is opened under water in order to prevent the access of air; and the substance, diluted with water, is distilled with an excess of sulphuric acid. The liquor collected in the receiver is saturated with carbonate of soda, and the solution evaporated to dryness; and, lastly, the residue is distilled with phosphoric acid, when the vale-

rianic acid forms an oily layer on the surface of the water in the receiver.

§ 1571. In order to extract valerianic acid from valerian root, it is sufficient to distil the root with a large quantity of water acidulated by sulphuric acid; a still larger quantity being obtained by using the following mixture:—1 kilog. of valerian root, 100 gr. of sulphuric acid, 60 gm. of bichromate of potassa, and 5 litres of water. This is owing to the fact that valerian contains an essential oil, *valerole*  $C_{12}H_{10}O_2$ , which is converted, by oxidizing reagents, into valerianic acid. The distillation should not be commenced until the mixture has macerated for 24 hours.

Valerianic or amylic acid is a colourless liquid, having a strong odour of valerian, and the density 0.937 at  $62.6^\circ$ , while it boils at  $175^\circ$ ; its equivalent  $C_{10}H_9O_3, HO$  corresponding to 4 volumes of vapour. It dissolves slightly in water, but in all proportions in alcohol and ether. The majority of the valerates are soluble, and the alkaline valerates crystallize with difficulty, while that of baryta forms small brilliant prisms. Valerate of silver is insoluble, and presents the formula  $AgO, C_{10}H_9O_3$ .

Valerianic acid is acted on by chlorine, even when protected from direct solar light, and is then converted into *trichlorinated valerianic acid*  $C_{10}H_6Cl_3O_3, HO$ . In order that the reaction may be complete, heat must be applied toward the close, and the current of chlorine must be kept up until no more chlorohydric acid is disengaged. If the action of chlorine be continued in the sun, *quadrichlorinated acid*  $C_{10}H_5Cl_4O_3, HO$  is obtained.

Valerate of baryta, distilled over the fire in a retort, yields a volatile, oleaginous product, which is purified by redistillation, collecting only the product which boils at  $212^\circ$ . The formula of this compound is  $C_{10}H_{10}O_2$ , and it is *amylic* or *valeric aldehyde*, which oxidizing reagents readily convert into valerianic acid; the transformation being effected even by the oxygen of the air in the presence of platinum-sponge.\*

#### ESSENTIAL OIL OF WINE, OR CENANTHIC ETHER $C_4H_5O, C_{14}H_{13}O_2$ .

§ 1572. There exists in wine an essential oil, to which the peculiar odour of wines, called their *bouquet*, has been chiefly attributed. It consists of a compound vinic ether, containing an acid called *cenanthic* (from *οἶνος*, vine, and *ἄνθος*, flower.)

When large quantities of wine are distilled, an oil volatilizes toward the close of the operation, which is a mixture of *vincenanthic*

\* Amylic ether is considered as the oxide of a radical *amyl*  $C_{10}H_{11}$ , in the same manner as ether is regarded as oxide of ethyl, which theory has gained much ground since amyl has been actually isolated.

Valerianic acid then assumes the formula  $(C_4H_5)C_2O_2, HO$ , or oxalic acid paired with a radical *valyl*  $C_6H_5$ , which Kolbe has isolated.

See the note to § 1401.—W. L. F.

*ether* and free *œnanthic acid*. As the œnanthic ether is much more volatile than the œnanthic acid, they may be imperfectly separated by distillation; the first products being much richer in œnanthic ether. In order to obtain pure œnanthic ether, the crude oil is shaken with a hot solution of carbonate of soda, which dissolves the free œnanthic acid, and toward the close it is heated to ebullition, so that the œnanthic ether may separate more readily and form an oily layer on the surface. After being decanted, and again subjected to the same treatment, it is dried over chloride of calcium and purified by distillation.

œNanthic ether is a colourless liquid, of a very penetrating smell of wine, and an acrid and disagreeable taste. It is insoluble in water, but dissolves readily in alcohol and ether. Its density is 0.862, it boils at  $446^{\circ}$ , and the density of its vapour is 10.48; its equivalent  $C_4H_5O, C_{14}H_{13}O_3$ , being therefore represented by 2 volumes of vapour. It is easily decomposed by a hot solution of caustic potassa, or soda, yielding alcohol and œnanthic acid which remains combined with the alkali. By decomposing the alkaline œnanthate by dilute sulphuric acid, the œnanthic acid collects on the surface of the liquid in the form of a colourless oil, which is merely washed with hot water, and then dried in vacuo.

At the ordinary temperature œnanthic acid has the consistence of butter, while it becomes very fluid at a higher temperature, and boils at about  $570^{\circ}$ . It does not sensibly dissolve in water, but it nevertheless reddens litmus. Alcohol and ether dissolve it freely. The distilled acid is anhydrous, and presents the formula  $C_{14}H_{13}O_3$ ; while, when in contact with water, it abstracts 1 equiv. from it and becomes monohydrated acid  $C_{14}H_{13}O_3.HO$ . By heating to  $302^{\circ}$  a mixture of 5 parts of sulphovinate of potassa and 1 part of monohydrated œnanthic acid, a vincœnanthic ether is obtained, which may be purified by a hot solution of carbonate of soda. If a mixture of wood-spirit, concentrated sulphuric acid, and œnanthic acid be heated, *methœnanthic ether*  $C_2H_5O, C_{14}H_{13}O$  is formed.

As vincœnanthic ether cannot be detected in the fresh juices of vegetables, it is probably a product of fermentation.

#### CAOUTCHOUC.

§ 1573. Caoutchouc is contained in the milky juice of several vegetables, where it exists in the form of small globules, suspended in an aqueous liquid, precisely in the same manner as the fatty globules in milk. The chief importations of caoutchouc are from Java and South America; and it is obtained from the *siphonia cahucha* and the *ficus elastica*. The milky sap of these trees contains about 30 per cent. of caoutchouc; and when left to itself, the globules of caoutchouc float on the surface, because they are lighter than water, and form a thick cream on it; which separation is more easily effected if the density of the water is increased by sea-salt.

In order to collect the caoutchouc, deep incisions are made into the base of the tree producing it, and the liquid which exudes is received in earthen vessels, whence it is transferred into bottles, which, when hermetically sealed, may be transported and preserved for a long time without undergoing any change. The greater part of the caoutchouc found in commerce is in the shape of pears, either smooth or covered with marks, and generally of a brown colour. The Indians make these pears by spreading successive layers of the milky juice, which they coagulate in the sun, over pyriform clay moulds; and when the caoutchouc is of sufficient thickness, they dip the mould in water to soften the earth, which is then emptied through the mouth of the caoutchouc bottle. The brown colour is owing to the deposition of the smoke during its desiccation over fire.

Pure caoutchouc must be obtained from the milky juice itself, by mixing it with 4 times its weight of water, and allowing it to rest for 24 hours, when the globules of caoutchouc float on the surface in the form of cream. This cream is removed, and by agitation is suspended with an additional quantity of water, of which the density is increased by a small quantity of sea-salt and chlorohydric acid; when, after some time, the caoutchouc again collects on the surface, and is again removed and washed, and so on, until the water will dissolve no more of it; after which the substance is compressed between paper and dried under the receiver of an air-pump. Caoutchouc, thus prepared, is a white, elastic substance, of the density 0.925, and containing 87.2 of carbon and 12.8 of hydrogen.

All the useful articles of caoutchouc, now so extensively applied in the arts, are manufactured from the pyriform substance, by very various mechanical processes, the description of which would be out of place. The elasticity and impermeability of caoutchouc render it valuable for many purposes in surgery, and it also finds frequent use in the laboratory of the chemist and physicist. It has recently been used for covering cloths and other stuffs, to render them water and air tight.

Caoutchouc is hard at a low temperature, but softens readily by heat, and at  $77^{\circ}$  possesses great flexibility; while it melts at about  $248^{\circ}$ , and then forms a viscous liquid, which does not recover its original condition for a very long time. If it be further heated, the liquid becomes more fluid, and remains indefinitely viscous even after cooling. Melted caoutchouc, diluted with a small quantity of some fatty oil, is used for greasing stopcocks. It burns with a brilliant and very smoky flame; and by heating it to distillation, it is converted into several essential oils, of different volatile powers, and which are themselves modified by redistillation.

Caoutchouc is insoluble in water and alcohol, although boiling water softens it and causes it to swell, but without dissolving it. Ether, the essential oils, and sulphide of carbon, on the contrary, dissolve it readily, and form solutions, which deposit, after sponta-

neous evaporation, on the objects to which they have been applied, an elastic and impervious coating of caoutchouc.\*

## GUTTA-PERCHA.

§ 1574. A substance of organic origin has lately been found, closely resembling caoutchouc in its chemical and physical properties, and called *gutta-percha*, which is used in the fabrication of bands to drive machinery, and several purposes which require great solidity united to a certain degree of flexibility. It is imported from India and China, and is probably the product of some vegetable, although as yet we have no accurate account of its origin.

Gutta-percha is of a grayish-white colour, of a consistence resembling that of horn, and not at all elastic; but it softens and becomes more elastic by an increase of temperature, its original hardness returning after cooling. It burns, like caoutchouc, with a brilliant and smoky flame. Water, alcohol, the acid or alkaline liquors, exert no action upon it; but ether and the essential oils first soften and then dissolve it. Its elementary composition differs but slightly from caoutchouc, for 87.8 of carbon and 12.2 of hydrogen have been found in it.†

## RESINS.

§ 1575. The name of *resins* has been given to certain solid substances, widely spread among vegetables, and which flow copiously from some of them in the state of solution in the essential oil. Resins are solid, non-volatile, sometimes colourless, most frequently of a yellow or brown tinge; insoluble in water, but dissolving readily

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\* The discoveries of Goodyear that caoutchouc may be modified in its properties by various processes, termed *vulcanizing*, are too important to pass over in utter silence. Charles Goodyear, of Connecticut, United States, discovered, by years of patient and laborious experiment, that sulphur heated with caoutchouc produced what he termed a *drying* effect upon the latter, rendering it more elastic, incapable of becoming hard by frost, insoluble in ether, the essential oils, &c. By a series of highly ingenious mechanical processes, the new fabric was made to imitate paper, every kind of leather, and various kinds of dry goods, still, however, retaining more or less of the original, valuable properties of the rubber. His more recent improvements consist in imparting to caoutchouc any required degree of hardness between its usually soft state and the hardness and elasticity of ivory, effected by an expansion of his sulphurizing process, and by the addition of materials to the caoutchouc. By this discovery of Goodyear, and through his enterprise and patient perseverance, a single vegetable product can be made to replace paper, leather, and dry goods, but with greater elasticity and durability,—to replace whalebone, horn, tortoise-shell, horn, and ivory.—*J. C. B.*

† Gutta-percha is similar in its origin and composition to caoutchouc, and yet presents very different external characters. The hardening effect produced by Goodyear's sulphuration of caoutchouc seems to convert the latter into a substance resembling gutta-percha in its properties, and enables us to comprehend how the same class of plants may produce substances of very different external properties. The uses of gutta-percha are rapidly extending.—*J. C. B.*

in absolute alcohol, which frequently deposits them, in the form of crystals, after evaporation. The majority of resins behave like weak acids, and form definite compounds with the alkalies and with other metallic oxides. We shall here describe only the resins of terpentine, which have, as yet, been most accurately investigated.

When the terpentine which exudes from the *pinus maritima* is distilled with water, the oil of terpentine distills with the water, while a substance called *colophony* remains, consisting of three resins, possessing acid properties, and to which the name of *pimaric*, *sylvic*, and *pinic acid* have been given. The elementary composition of these three acids is exactly the same, corresponding to the formula  $C_{40}H_{30}O_4 = C_{40}H_{29}O_3.HO$ .

Pimaric acid predominates greatly over the other two acid resins, and colophony appears sometimes to be wholly constituted of it. In order to obtain it, powdered colophony is treated several times with a mixture of 5 or 6 parts of alcohol and 1 part of ether, when the sylvic and pinic acids are dissolved, while the greater portion of the pimaric acid remains as a residue, and is purified by being crystallized repeatedly from boiling alcohol. Pimaric acid dissolves very readily in ether, while it requires 10 parts of cold and its own weight of boiling alcohol for solution. It melts at about  $257^{\circ}$ , and then undergoes an isomeric modification, which is easily recognisable by dissolving it in cold alcohol, of which it then only requires 1 part. However, this modification is not fixed, since, after a certain time, the pimaric acid is regenerated, with its original properties, in the alcoholic solution, and the greater portion of it is deposited in crystals.

Crystallized pimaric acid is after a time spontaneously converted into pinic acid, when it is soluble in its own weight of alcohol, and does not assume any crystalline form.

By distilling pimaric acid, an oleaginous substance is condensed and congeals in the neck of the retort; and it is purified by dissolving it in boiling alcohol, whence it is deposited in the form of crystalline lamellæ. This substance is identical with sylvic acid, of which we mentioned the presence in colophony, differing from pimaric acid by its crystalline form, melting at nearly the same temperature of  $257^{\circ}$ , and dissolving in 8 or 10 times its weight of alcohol.

A great number of resins are found in commerce, which are generally called by the name of the vegetable from which they are derived; and the chemical properties of all of them are analogous to those of resins of terpentine.

Resins yield by distillation very complicated products: carburetted hydrogens, which burn with a brilliant flame, and are used as illuminating gases; besides essential and fixed oils. The following products have been separated:

*Retinaphtha*  $C_{14}H_8$ , an oil boiling at  $226.6^\circ$ .

*Retinyl*  $C_{18}H_{12}$ , “ “  $302.0^\circ$ .

*Retinole*  $C_{12}H_6$ , isomeric with benzene, boiling at  $464.0^\circ$ .

*Retisterin*, isomeric with naphthalin, a crystalline substance melting at  $149^\circ$ , and boiling at  $617.0^\circ$ .

#### SULPHURETTED ESSENTIAL OILS.

§ 1576. Only two sulphuretted essential oils are as yet accurately known: oil of mustard, and oil of garlic; while their number will, without doubt, be greatly increased hereafter.

#### OIL OF GARLIC $C_6H_5S$ .

§ 1577. This essential oil is obtained by distilling cloves of garlic with water, when an extremely fetid brown-coloured oil passes over, which is decanted, and, after distillation in a salt-water bath, is rectified over potassium until it is no longer acted on by this metal. Oil of garlic is a colourless liquid, of a repulsive odour, less dense than water, distilling without alteration, and presenting the formula  $C_6H_5S$ . It has been called *sulphide of allyl*, because it has been considered as a compound of sulphur with a carburetted hydrogen  $C_6H_5$ , or *allyl*. This oil throws down precipitates with several metallic solutions: thus, if a concentrated solution of it be mixed with an equally concentrated solution of chloride of mercury, a white precipitate is formed, which, when purified by being washed in alcohol, presents the formula  $(HgS)_2, C_6H_5S + (HgCl)_2, C_6H_5Cl$ . When alcoholic solutions of oil of garlic and bichloride of platinum are mixed together, and the liquid is diluted with water, a yellow precipitate is formed, of which the composition corresponds to the formula  $3(PtS_2, C_6H_5S) + PtCl_2, C_6H_5Cl$ . When an alcoholic solution of oil of garlic is added to nitrate of silver, a precipitate of sulphide of silver is obtained, mixed with a white crystalline compound, which is deposited from a solution in boiling water, when kept in the dark, in the form of brilliant white crystals, of a composition corresponding to the formula  $AgO, NO_5, C_6H_5O$ , which may be considered as formed by the combination of 1 equivalent of nitrate of silver with 1 equivalent of oil of garlic, the equivalent of sulphur in the latter having been replaced by 1 equivalent of oxygen. By treating this crystalline substance with ammonia, the compound  $C_6H_5O$ , called *oxyde of allyl*, is separated, in the form of a volatile, colourless oil, of a disagreeable odour, which combines directly with nitrate of silver, reproducing the crystalline compound of which we have just spoken.



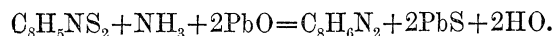
OIL OF BLACK MUSTARD  $C_8H_5NS_2$ 

§ 1578. This oil does not exist already formed in mustard-seed, but is developed in it, in the presence of water, by a kind of fermentation taking place between the substances contained in the seed, to which we shall presently recur. The fatty oil contained in the mustard-seed is extracted by means of a press; when the cake being moistened with water, and left to itself for several hours, the seed, at first inodorous, soon exhales the pungent smell of mustard. It is then distilled with water, when a yellow oil, denser than water, passes over with the aqueous vapours. By a second distillation with water, it loses colour sensibly, but as it still contains foreign substances, it is distilled in a retort furnished with a thermometer, and the liquid which distills below  $293^\circ$  is separated, the temperature being arrested at this point, when pure oil of mustard passes over.

Oil of mustard is a colourless oil, boiling at  $293^\circ$ , and furnishing vapours which irritate the eyes and nose, and show the density 3.4, its equivalent  $C_8H_5NS_2$  corresponding to 4 volumes of vapour. It is very soluble in alcohol and ether, but insoluble in water, and it exerts no rotatory power. Its formula  $C_8H_5NS_2$  may be written  $C_6H_5S, C_2N, S$ , which constitutes oil of garlic  $C_6H_5S$  and sulphocyanogen; and in fact, the constitution of oil of mustard must be thus considered, for if it be treated with monosulphide of potassium, oil of garlic  $C_6H_5S$  is obtained by distillation, while the liquid contains sulphocyanide of potassium. If the vapour of oil of mustard be passed over a mixture of lime and caustic soda, heated to  $248^\circ$ , oxide of allyl  $C_6H_5O$  is obtained, and the residue contains sulphocyanides.

§ 1579. Oil of mustard yields, either with ammoniacal gas or with liquid ammonia, a crystallized compound, *thiosinammin*  $C_8H_5NS_2NH_3$ , which is a true alkaloid. This substance being redissolved in boiling water, the liquor, when bleached by animal black, deposits, by evaporation, the thiosinammin, in the form of prismatic crystals, of a brilliant white colour. It dissolves in chlorohydric acid, forming an uncrystallizable compound; while, by adding bichloride of platinum to the solution, a yellow crystalline precipitate is formed, of which the formula is  $(C_8H_5NS_2, NH_3), HCl + PtCl_2$ . Thiosinammin dissolves also in sulphuric, nitric, and acetic acids, but the compounds do not crystallize.

When heated with oxide of lead or mercury, it parts wholly with its sulphur, and a new alkaloid  $C_8H_6N_2$ , called *sinammin*, is formed:

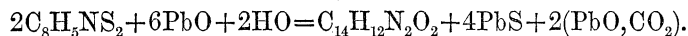


Powdered thiosinammin is mixed with freshly precipitated and moist hydrated protoxide of lead, and is heated over a water-bath

until the filtered liquid is no longer blackened by the addition of potassa; after which it is heated several times with boiling alcohol, to dissolve the sinammin, leaving, after evaporation, a syrupy mass in which crystals are developed.

Sinammin has a strongly alkaline reaction, but forms only a small number of crystallizable salts and its chlorohydric solution yields, with the bichloride of platinum, a flaky yellow precipitate, of the formula  $C_8H_6N_2 \cdot 2HCl + 2PtCl_2$ .

If oil of mustard be digested with hydrated oxide of lead, until an additional quantity of the oxide ceases to turn black, and it be then treated with boiling water, a new substance  $C_{14}H_{12}N_2O_2$ , called *sinapolin*, is dissolved, which also possesses basic properties, the reaction from which it arises being expressed by the following equation:



Synapolin crystallizes from its aqueous solution in spangles of a grayish lustre, and turns litmus blue, while its solution in chlorohydric acid yields a crystalline precipitate with chloride of mercury.

#### *Myronic Acid and Myrosin.*

§ 1580. Black mustard-seed contains an acid substance, *myronic acid*, combined with potassa, which, by the assistance of water and a peculiar ferment, called *myrosin*, also contained in the seed, is converted into oil of mustard by a peculiar fermentation, called *sinapic fermentation*. In order to extract the myronate of potassa, black mustard-seed, previously freed from its fatty oil by pressure, is heated with alcohol to  $185^\circ$ ; when the ferment, myrosin, in this way coagulates and becomes inactive. The substance is again expressed and heated with tepid water, which dissolves the myronate of potassa; and by adding alcohol to this new solution, some mucilaginous substances are coagulated, when the liquid, after evaporation, deposits crystals of myronate of potassa.

By pouring tartaric acid into a concentrated solution of myronate of potassa, the greater part of the potassa is precipitated, and a very acid liquor remains, which leaves, after evaporation, an uncrySTALLIZABLE syrupy substance. The composition of myronic acid is unknown.

Myrosin is separated by exhausting white mustard-seed with cold water, evaporating the filtered liquid at a low temperature, and adding alcohol, which precipitates the myrosin. Myrosin cannot be extracted from black mustard-seed, because it forms oil of mustard as soon as it is moistened with water. No other known ferment can be substituted for myrosin in the sinapic fermentation.

## OF SOME IMPORTANT PRODUCTS WHICH ARE FORMED DURING THE DISTILLATION OF ORGANIC SUBSTANCES.

§ 1581. We shall include in this chapter some important substances produced by the distillation of organic matter, which have not yet been, with certainty, appended to any great series. We shall add the native hydrocarburetted essential oils, known under the name of *naphtha* and *petroleum*, which probably arise in the same manner from the bosom of the earth.

NAPHTHALIN  $C_{20}H_8$ .

§ 1582. This remarkable substance is formed by the decomposition of a great number of organic substances at a high temperature, a considerable quantity of it being produced in the manufacture of illuminating gas from bituminous coal. Adulterated with an oily substance and lampblack, naphthalin is deposited in crystals on the sides of the pipes which convey the gas from the retorts; and it must be removed, from time to time, to prevent their becoming completely choked; and in the laboratory, it is generally extracted from these deposits. The most simple method consists in employing the process described (§ 1527) for the extraction of benzoic acid, by sublimation from the resin of benzoin, the naphthalin thus obtained being nearly pure; and to make it perfectly so, it is dissolved in boiling alcohol, whence it is again deposited, in crystals, on cooling.

Naphthalin crystallizes in beautiful rhomboidal laminae, of a white colour and greasy lustre; has a peculiar, very persistent odour; melts at  $174.2^\circ$ , and boils at  $413.6^\circ$ , the density of its vapour being 4.53, and its equivalent  $C_{20}H_8$  corresponding to 4 volumes of vapour. Hot water dissolves a very small quantity of it, for water, heated with naphthalin, becomes slightly cloudy on cooling. Alcohol dissolves one-fourth of its weight of it, while ether and the essential oils dissolve it more freely.

§ 1583. Chlorine acts readily on naphthalin, which first becomes liquid under its action, but again solidifies if it be prolonged. If the substance be then expressed between tissue-paper and crystallized in ether, a homogeneous substance of the formula  $C_{20}H_8Cl_4$  is obtained, which may be considered as a combination of 1 equivalent of naphthalin and 4 equivalents of chlorine. The formula of the liquid which precedes the formation of this crystalline compound is  $C_{20}H_8Cl_2$ ; and it results from the combination of 1 equivalent of naphthalin with 2 equivalents of chlorine. The formula of the crystalline compound may be written  $C_{20}H_6Cl_2 \cdot 2HCl$ , being considered as a compound of 1 equivalent of bichlorinated naphthalin  $C_{20}H_6Cl_2$  with 2 equivalents of chlorohydric acid. In fact, the substance is in this manner decomposed by heat, chlorohydric acid being disengaged, while bichlorinated naphthalin  $C_{20}H_6Cl_2$  condenses in the form of a colourless liquid. The liquid substance  $C_{20}H_8Cl_2$  being also

decomposed by heat into chlorohydric acid, and into monochlorinated naphthalin  $C_{20}H_7Cl$ ; its formula may therefore be written  $C_{20}H_7Cl, HCl$ . These are not the only substances which may be derived from naphthalin by the action of chlorine, since a great numbers of others exist, which are obtained by subjecting the first two to various reagents, or by causing chlorine to act on the products they yield by distillation. We shall merely indicate the formulæ of the principal of these substances:

Naphthalin.....	$C_{20}H_8$ ,
Monochlorinated naphthalin .....	$C_{20}H_7Cl$ ,
Bichlorinated “ .....	$C_{20}H_6Cl_2$ ,
Trichlorinated “ .....	$C_{20}H_5Cl_3$ ,
Quadrichlorinated “ .....	$C_{20}H_4Cl_4$ ,
Sesquichlorinated “ .....	$C_{20}H_2Cl_6$ ,
Perchlorinated “ .....	$C_{20}Cl_8$ .

With bromine have been obtained

Monobrominated naphthalin .....	$C_{20}H_7Br$ ,
Bibrominated “ .....	$C_{20}H_6Br_2$ ,
Tribrominated “ .....	$C_{20}H_5Br_3$ ,
Quadribrominated “ .....	$C_{20}H_4Br_4$ .

By the successive action of bromine and chlorine,

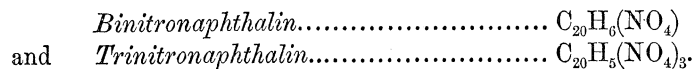
Bromobichlorinated naphthalin.....	$C_{20}H_5BrCl_2$ ,
Bibromobichlorinated “ .....	$C_{20}H_4Br_2Cl_2$ ,
Bromotrichlorinated “ .....	$C_{20}H_4BrCl_3$ ,
Bibromotrichlorinated “ .....	$C_{20}H_3Br_2Cl_3$ .

To which may be added the more complex groupings, considered either as compounds with chlorine or bromine, of the original naphthalin or chlorinated or brominated naphthalins, or as chlorohydrates of chlorinated naphthalin, from which two ways of examining them we shall write their formulæ:

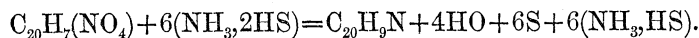
$C_{20}H_8Cl_2$ .....	or .....	$C_{20}H_7Cl, HCl$ ,
$C_{20}H_6Cl_2, Cl_2$ .....		$C_{20}H_5Cl_3, HCl$ ,
$C_{20}H_6Br_2, Cl_2$ .....		$C_{20}H_5Br_2Cl, HCl$ ,
$C_{20}H_5Br_3, Br_2$ .....		$C_{20}H_4Br_4, HBr$ .
$C_{20}H_8Cl_4$ .....		$C_{20}H_6Cl_2, 2HCl$ ,
$C_{20}H_7Cl, Cl_4$ .....		$C_{20}H_5Cl_3, 2HCl$ ,
$C_{20}H_4Br_2Cl_2, Br_4$ .....		$C_{20}H_2Br_4Cl_2, 2HBr$ .

§ 1584. Nitric acid reacts readily on naphthalin at the boiling point, converting it rapidly into an oil which solidifies on cooling, and should be purified by several crystallizations in alcohol. Its

formula being  $C_{20}H_7(NO_4)$ , it may be considered as naphthalin in which 1 equiv. of hydrogen is replaced by 1 equiv. of the compound  $NO_4$ . By continuing the action of the nitric acid, we obtain successively



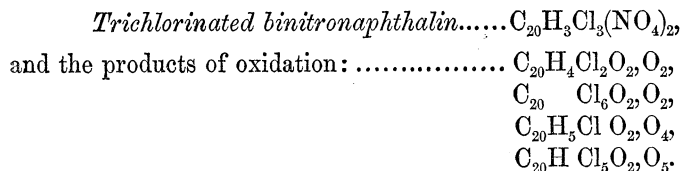
By causing sulphhydrate of ammonia to act on an alcoholic solution of mononitronaphthalin  $C_{20}H_7(NO_4)$ , an organic base is obtained, *naphthalidam*  $C_{20}H_9N$ :



This substance crystallizes in white needles, melting at  $86^\circ$ , and boiling at about  $570^\circ$ , without alteration, which combine with the acids and form crystallizable salts, the formula of the chlorohydrate being  $C_{20}H_9N, HCl$ , and that of the sulphate  $(C_{20}H_9N, HO), SO_3$ .

Under the same circumstances, binitronaphthalin  $C_{20}H_6(NO_4)_2$ , and the trinitronaphthalin  $C_{20}H_5(NO_4)_3$ , yield other alkaloids  $C_{20}H_8N_2$ ,  $C_{20}H_7N_3$ .

By causing nitric acid to act on chlorinated naphthalins, there result either substitutions of the compound  $NO_4$  for hydrogen, or products of oxidation in which the molecule of naphthalin is modified by the substitution of oxygen in the place of hydrogen; and in this manner have been obtained

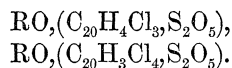


It will be seen that from no carburetted hydrogen are more numerous products derived than from naphthalin; which probably arises from the fact that no other one has been so carefully examined in this point of view.

§ 1585. Concentrated sulphuric acid acts readily on naphthalin, and yields acid compounds. By heating naphthalin to about  $194^\circ$  with concentrated sulphuric acid, it dissolves in it, and forms a syrupy liquid, generally reddish, which, when exposed to a moist air, sets in a crystalline mass, readily soluble in water, producing an acid liquid which forms, with carbonate of lead, two salts unequally soluble in alcohol. The acid of which the salt of lead is more soluble in alcohol is by far the more abundant, and has been called *sulphonaphthalic acid*; the general formula of its dried salt being  $RO$ ,  $(C_{20}H_7S_2O_5)$ . The other acid has received the name of *sulphonaphthalic acid*, but its composition is not exactly known.

By causing concentrated sulphuric acid to act on trichlorinated

and on quadrichlorinated naphthalin, there result acids perfectly analogous to sulphonaphthalic acid, forming salts of the general formulæ, when dried,



By substituting anhydrous sulphuric for monohydrated sulphuric acid, two neutral crystallizable substances are obtained in addition to the same acid compounds: *sulphonaphthalin*, of which the formula is  $\text{C}_{20}\text{H}_3\text{SO}_2$ , and *sulphonaphthalide*, the composition of which appears to correspond to the formula  $\text{C}_{24}\text{H}_{10}\text{SO}_2$ . These substances are generally accompanied by a red colouring matter, of which the composition is not yet exactly known.

### *Paraffin.*

§ 1586. A small quantity of this substance is found among the products of distillation of bituminous coals, together with a great number of organic substances; and it is concentrated in the substances which volatilize last, when these products are subjected to redistillation. In order to extract it, the substance is heated with concentrated sulphuric acid, which carbonizes the greater portion of the substances mixed with the paraffin, when, if the liquid be allowed to rest, at a temperature of  $122^\circ$  or  $140^\circ$ , the pure paraffin forms an oily layer on the surface, which solidifies on cooling. The substance is expressed several times between tissue-paper, which absorbs the oily portions, and it is purified by solution in boiling alcohol, or in a mixture of alcohol and ether, whence it is deposited, on cooling, in the form of brilliant spangles of a greasy lustre.

A large quantity of paraffin may be obtained by distilling a mixture of wax and lime, when the oily product which solidifies on cooling, after being expressed between tissue-paper, furnishes pure paraffin by crystallization in alcohol or in ether.

Paraffin melts at  $116.6^\circ$  and boils at about  $700^\circ$ , while, if it is not carefully heated, a portion of it is decomposed and yields gaseous products. It is distinguished by great stability, since concentrated sulphuric acid, at a temperature not exceeding  $212^\circ$ , ordinary nitric acid, and chlorine, exert no action upon it, to which property it owes its name, (from *parum affinis*.) Paraffin burns in the air with a brilliant flame, and very good candles are made of it. 100 parts of boiling alcohol dissolve about 3.5 of it, nearly all of which is deposited on cooling.

The name of *eupione* has been given to volatile oils obtained, in greater or less quantity, in the preparation of paraffin, which are mixtures of various carburetted hydrogens, analogous to those constituting petroleum.

PHENIC ACID, PHENOLE, OR CARBOLIC ACID  $C_{12}H_8O, HO$ .

§ 1587. These various names are given to a product extracted from coal-tar, by distilling the oily part of the tar and collecting separately the portion which passes over between  $300^{\circ}$  and  $400^{\circ}$ . The liquid distilled between these two degrees is shaken several times with a very concentrated solution of caustic potassa, to which fragments of hydrate of potassa are added, when the oil disengages a disagreeable odour, and sets into a crystalline mass. Water being then added, and the whole heated to boiling, the liquid separates into two layers: a light, oily layer, which is removed, and a heavier, aqueous liquid, which is treated with chlorohydric acid. The oil which is thus separated by rising to the surface is decanted, digested over chloride of calcium, and distilled several times. This oil, which is phenic acid, and becomes solid at a low temperature, is also formed in the distillation of salicylic acid with lime, and in that of benzoïn.

Phenic acid constitutes, at the ordinary temperature, a white crystalline compound, melting at about  $95.0^{\circ}$ , and boiling at  $370.4^{\circ}$ ; of the density 1.065 at  $64.4^{\circ}$ ; slightly soluble in water, and dissolving in all proportions in alcohol and ether. It combines with potassa to a crystalline salt  $KO, C_{12}H_5O$ , and forms analogous compounds with baryta and lime. It reduces several metallic salts, particularly the salts of silver and mercury.

Chlorine acts readily on phenic acid, and the following phenic acids have thus been obtained:

Bichlorinated .....  $C_{12}H_3Cl_2O, HO$ ,  
and Trichlorinated .....  $C_{12}H_2Cl_3O, HO$ .

Bromine forms analogous products.

Nitric acid also acts on phenic acid, and yields successively *binitrophenic acid*  $C_{12}H_3(NO_2)_2O, HO$ , and *trinitrophenic acid*  $C_{12}H_2(NO_2)_3O, HO$ ; which two products are generally prepared by attacking directly, by nitric acid, the portion of oil of coal-tar which distils between  $354^{\circ}$  and  $374^{\circ}$ , when a very energetic reaction ensues, furnishing a brown mass, which is washed with cold water and dissolved in ammoniacal water heated to boiling. The liquid deposits, on cooling, *binitrophenate of ammonia*, which is to be purified by several crystallizations; and which, by decomposition with chlorohydric acid, yields binitrophenic acid. This acid, which crystallizes in right-angled prisms, with a rectangular base, and of a slightly yellowish colour, is suddenly decomposed by heat. It dissolves slightly in boiling water, and is wholly deposited from it on cooling, while alcohol and ether dissolve it largely.

Boiling nitric acid acts readily on binitrophenic acid, and converts it into *trinitrophenic acid*  $C_{12}H_2(NO_2)_3O, HO$ , which has been known for a long time under different names; having been called *Welter's bitter*, *nitrocarbonic acid*, *picric acid*, etc. It is obtained

by the action of nitric acid on the most diversified organic substances, particularly on nitrogenous substances of animal origin, such as silk, fibrine, and animal tissues. Salicin treated with nitric acid yields a large quantity of trinitrophenic acid, and we shall see that it is also obtained in treating indigo by the same acid. It crystallizes in brilliant yellow prisms, is but slightly soluble in cold, but largely so in hot water, while alcohol and ether dissolve it freely. It forms yellow crystallizable salts with bases which detonate when heated.

CREASOTE  $C_{28}H_{16}O_3$ .

§ 1588. A liquid substance, called *creasote*, and possessing some interest in being used to allay toothache, is extracted from wood-tar and pyroligneous acid, by a long and complicated process. The wood-tar is distilled until a pitchlike mass alone remains, when the distilled liquid separates in the receiver into three layers, the lower of which, containing the creasote, is saturated with carbonate of soda; after which the supernatant oil is decanted and again distilled; the first products, which are lighter than water, being rejected, while the heavier oil is collected and again distilled. This oil is then shaken several times with a weak and hot solution of phosphoric acid, washed until it gives off no more acid, and treated with an alkaline solution of the density 1.12, when the creasote leaves the oil, and dissolves in the alkaline liquid, which is separated and exposed for some time to the air, to oxidize a foreign substance which discolours the liquid. Lastly, the solution, after being saturated with phosphoric acid, is distilled, when the creasote volatilizes with the water and separates in the receiver in the form of an oily layer.

Creasote is a colourless, oleaginous liquid, of a penetrating and disagreeable odour and an acrid and burning taste; cauterizing the organic tissues, coagulating albumen, and preventing the putrefaction of meat. It boils, without change, at about  $390^{\circ}$ , and is insoluble in water, but readily so in alcohol and ether. It forms, with potassa and soda, crystalline compounds, from which acids separate it without change; and its composition corresponds to the formula  $C_{28}H_{16}O_4$ .

An alcoholic solution of creasote is used in medicine.

NAPHTHA, OR PETROLEUM.

§ 1589. In many countries, odoriferous oils exude from the ground, accompanied generally by hot or cold water, and sometimes by combustible gases; and when such liquids are collected in natural or artificial reservoirs, the oil floats on the surface. The general name of *petroleum* is given to these oils, the nature of which is evidently very diversified, for some of them distil wholly without change, while others leave a considerable residue of fixed oil, which is decomposed by heat. The most abundant springs of petroleum



are in the neighbourhood of Baku in Persia, where jets of combustible gas, copious enough to enable the inhabitants to use it for cooking their food, issue simultaneously from fissures in the ground; and some springs of petroleum are also found at Amiano, in the Duchy of Parma. Petroleum is purified by distillation with water, and the product is known in commerce by the name of *oil of naphtha*, or *oil of petroleum*.

Oil of naphtha, which presents the density of about 0.84, and gives a peculiar odour, contains no oxygen, and appears to be formed by the mixture of several carburetted hydrogens. If it be distilled in a retort furnished with a thermometer, ebullition is found to commence when the thermometer marks  $250^{\circ}$  to  $284^{\circ}$ , while the temperature gradually rises, and the last portions do not distil below  $570^{\circ}$ . If the products of distillation be collected separately, the most volatile is a liquid boiling at about  $194^{\circ}$ , after which numerous products pass over, boiling at higher and higher temperatures, while it has hitherto been impossible to separate a liquid presenting a constant boiling point, mixtures only having been obtained. The composition of the most volatile products correspond approximately to the formula  $\text{CH}_4$ , and they are isomeric with olefiant gas, while the less volatile products contain less hydrogen.

The essential oils which form petroleum are remarkable for their resistance to chemical agents, since they are scarcely affected by concentrated sulphuric and nitric acids; and they are used in the laboratory for the preservation of potassium, (§ 426.)

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### THE FATS.

§ 1590. The name of *fats* is commonly assigned to substances of organic origin, liquid or solid, but melting at a very low temperature, which, when spread in a liquid state on paper, render it translucent, and make permanent stains on it, known by the name of grease-spots; while the chemist defines fats by certain chemical properties, and, particularly, by their manner of composition, as shall subsequently be shown.

Fatty substances are found both in the vegetable and animal kingdoms, and seem to be identical in both; which has led some physiologists to the opinion that animals merely assimilate to themselves those which exist in vegetables, without their undergoing any chemical change. Although we shall reserve for the close of this work the study of the principal substances constituting the animal economy, we shall not, in this place, separate the fatty substances of the two kingdoms.

Vegetable fats are generally fluid at the ordinary temperature, while several of them coagulate and solidify, more or less perfectly,

at a low temperature. They are completely liquid only at a high heat, and at the ordinary temperature possess a certain degree of viscosity, called an *oily consistence*. The fat of warm-blooded animals is solid, its firmness varying according to the position it occupies in the body of the animal; while that of fishes and cold-blooded animals in general is fluid.

In plants, fat is found chiefly in the seeds and pericarp of the fruit, in the form of small drops which fill peculiar cells, and also exists in the shape of a waxlike substance on the surface of the leaves and bark. The proportion existing in seeds is often very considerable: thus, flaxseed contains about 20 per cent. of oil, and rapeseed 35 to 40, while the seed of *ricinus communis*, which furnishes castor-oil, contains as much as 60. The oil is generally extracted merely by expressing the seeds, but in order to render it more fluid they are heated, and then compressed between hot plates. When the proportion of oil is smaller, fermentation is sometimes resorted to for the destruction of a portion of the organic substances and in order to break up the fruit. Lastly, in the laboratory, solvents are sometimes used, chiefly ether, which is then driven off by evaporation.

Animal fat may be obtained either mechanically or by the action of heat. In order to purify it in the laboratory, it is generally dissolved in ether; but it must not be forgotten that this liquid can also dissolve some of the foreign substances mixed with the fat. The melting point of fat varies from  $23^{\circ}$  to  $140^{\circ}$ , while at temperatures above  $480^{\circ}$  they yield copious and very acrid fumes, but do not distil without alteration, whence they are called *fixed oils*. At an intense heat they are wholly decomposed, and produce gases of great illuminating power.

§ 1591. Oils generally absorb oxygen from the air, but in very various proportions; and while some absorb but small quantities of it without sensibly changing in appearance, merely acquiring a disagreeable smell, when they are said to *become rancid*, others absorb larger proportions of oxygen, become covered with a coating of a resinous appearance, and are finally completely solidified; and these are called *drying-oils*, the only ones which can be used in painting. Linseed, nut, hemp, poppy, and castor-oil are drying-oils, while some fish-oils appear to possess the same property. The fat of warm-blooded animals, the oil of almonds, olive-oil, rapeseed-oil, &c. are not drying-oils.

The chemical action which produces the solidification of drying-oils is sometimes limited to a simple combination with oxygen; as in the case with linseed-oil, which absorbs large quantities of oxygen without disengaging any gas; but more frequently carbonic acid, and sometimes hydrogen, is evolved. Absorption goes on slowly at first, but subsequently becomes more rapid, especially when the oil is spread over a large surface or on porous bodies. Drying-oils

dry more quickly when they have been previously boiled with litharge or peroxide of manganese; in which case they contain a small quantity of these metallic oxides in solution.

§ 1592. The greater part of animal fats is formed of several proximate principles united in indefinite proportions; and of which chemists have distinguished only three: *stearin*, *margarin*, and *olein*. These principles behave, in chemical reactions, like compounds of the same substance, *glycerin*, with a fatty acid, peculiar to each of these principles. Stearin and margarin, to which beef and mutton fat owe their solidity, are converted into glycerin, and two fatty acids, which are *stearic acid* for stearin, and *margaric acid* for margarin; while olein, to which fats owe their oleaginous character, is transformed into glycerin and *oleic acid*. In several fatty substances, such as butter, we find, in addition, small quantities of peculiar fatty matters, called *butyrin*, *caprin*, and *caproin*, which may be considered as compounds of glycerin with volatile acids, differing in each of these substances, and which have been called *butyric*, *capric*, and *caproic acids*. We have shown that butyric acid is formed in a peculiar fermentation of sugar; and it will now soon be seen that the same acid arises, as also capric and caproic acids, from the action of nitric acid on stearin, margarin, and olein. The fat of the goat contains, in addition to the ordinary immediate principles, a small quantity of a peculiar fat, called *hircin*, which behaves like a compound of glycerin and a peculiar volatile acid, *hircic acid*. Lastly, another fatty substance is found in fish-oils, which may be considered as a compound of glycerin and a peculiar acid, called *phocenic*, appearing to be identical with valerianic acid.

A peculiar fat substance is extracted from the head of the sperm whale, called *spermaceti*, the constitution of which is very different from that of other animal fats, since it does not contain glycerin, but in its stead another neutral substance, called *ethal*; while the fat acid which is combined with the ethal has received the name of *ethalic acid*.

Lastly, the various kinds of wax, which should be classed among the fats, from the definition given of the latter, (§ 1590,) differ completely from it in their chemical composition, as shall presently be shown.

§ 1593. Stearic, margaric, and oleic acids are weak acids, which are displaced from their compounds by a majority of the other acids; and they are insoluble in water, but soluble in alcohol, and very feebly in ether. They are less easily melted than the proximate fatty principles which produced them, and they do not distil without alteration under the ordinary pressure of the atmosphere. They are then decomposed at a temperature above 570°, yielding very complicated products; but they may be distilled in vacuo, because the distillation is then effected at a much lower temperature.

§ 1594. The chemical operations by which natural fat substances

are converted into glycerin and fat acids are known by the general name of *saponification*. They are various; and the saponification of fats may be effected either by alkalies or by powerful acids, or by the action of heat alone.

If fats be heated to a temperature of  $570^{\circ}$ , in an apparatus traversed by a current of steam, under a pressure inferior to that of the atmosphere, the glycerin is converted into several products soluble in water; while the fat acids, set free, distil without alteration; thus furnishing an example of saponification by heat alone.

The action of hot alkaline lixiviæ decomposes fats and oils into glycerin, which dissolves in the aqueous liquid, and into fat acids, which combine with the alkali and form salts, commonly called *soaps*, which are insoluble in the alkaline liquor, but readily dissolve in a sufficient quantity of water. This operation, called *saponification by bases*, may be effected not only by alkaline bases, such as potassa, soda, and ammonia, but also by other metallic oxides which possess powerful basic properties, such as baryta, strontia, lime, and the protoxides of lead and zinc. The other metallic oxides no longer produce the saponification of fats, that is, their decomposition into glycerin and fat acids; while they may combine with the isolated fat acids and form insoluble soaps. Water is generated during saponification, for the united weight of the glycerin and fat acids is greater than the weight of the original fat. The neutral alkaline carbonates can also effect the saponification of fats, in which case they part with one-half of their alkali, which produces saponification, while the other half retains all the carbonic acid in the shape of bicarbonate; carbonic acid being disengaged only if heat is applied, because the bicarbonate is then decomposed.

Powerful acids, such as sulphuric, also effect the saponification of fats; and if the proportion of acid be not very great, the fat acid is isolated, the glycerin combining with the animal acid to form a compound acid. If the weight of the mineral acid exceed the half of that of the fat acid, it often combines with the latter, producing *sulphoglyceric*, *sulphostearic*, *sulphomargaric*, and *sulpholeic acids*. Smaller quantities of sulphuric acid are however sometimes used to purify the oils intended for burning in lamps, in which case the acid selects the foreign substances more easily acted on, contained in the oils, dissolving them, and effecting only an insensible saponification.

§ 1595. No fatty substance is soluble in water, which does not even moisten them; while they are somewhat soluble in absolute alcohol and wood-spirit, ether and the essential oils dissolving them much more freely. The liquid fats are the best solvents of solid fats. We have seen that natural fats are rarely simple, nearly always mixtures or indefinite compounds of various different fatty substances, which are separated only with the greatest difficulty. When the fat is solid, it is sufficient to melt it, and allow it to cool slowly, to observe in it the forming of solid lumps, the nature of

which differs from the liquid part. So again, certain fatty oils, olive-oil, for example, deposits, by slow cooling, more or less copious flocculi, which differ from the liquid portion; and by expressing these solidified portions between tissue-paper, a large quantity of interstitial liquid oil can be separated, furnishing a mixture of stearin and margarin, adulterated merely with a small quantity of olein. The proportions of stearin and margarin in the substances expressed vary according to the nature of the original fats. When they are yielded by mutton or beef fat, or lard, they are composed almost wholly of stearin; while, if furnished by human fat or olive-oil, they consist chiefly of margarin. These substances may be more perfectly isolated by a proper use of solvents.

The immediate fluid constituent of animal fats, olein, is still more difficult to isolate, the oil which flows from the compression of such fats being olein saturated with stearin or margarin. The most fluid vegetable oils are themselves olein, containing more or less stearin and margarin in solution; and by cooling them gradually and decanting the fluid, a large portion of the solid constituent may be separated; or the oil may also be shaken with alcohol, which dissolves the olein much more freely than the stearin and margarin, and the alcoholic solution may be evaporated: but all these processes never effect a perfect separation. It is moreover highly probable that stearin, margarin, and olein are not merely mixed in the majority of fats, and that they are in the state of indefinite compounds.

Olein does not appear to be identical in the various vegetable oils, since several chemical experiments seem to prove that it differs in the drying and non-drying oils. If, for example, a non-drying oil, such as olive-oil, be agitated with a small quantity of hyponitric acid, or with a solution of subnitrate of mercury, which contains hyponitric acid, the oil becomes completely solid after some time, and is converted into a crystalline substance, *elaidin*. Drying-oils do not possess this property, which thus furnishes a test, applicable to commercial purposes, of the purity of olive-oil, which is frequently adulterated with other vegetable oils, and particularly with poppy-oil.

Fat acids which are capable of crystallization may be obtained in a state of purity, and since they at the same time form a great number of definite compounds, their properties and chemical composition have been more accurately ascertained than those of the fats which furnish them. Nevertheless, uncertainties still exist, on account of the very high value of their chemical equivalents; the smallest errors in analyses corresponding to 1 or several equivalents of simple elements, and sufficing to change the formulæ.

We shall examine only the most important and most common fatty substances, commencing with the study of glycerin, which is an essential and constant principle of the majority of these substances.

*Glycerin*  $C_6H_7O_5, HO$ .

§ 1596. The most simple method of preparing glycerin consists in heating fats with protoxide of lead, in the presence of water, when saponification is soon effected, an insoluble soap of lead being formed, while the glycerin remains dissolved in the water. The aqueous solution is subjected to a current of sulphydric gas, which precipitates a small quantity of oxide of lead dissolved in it in the state of sulphide; after which it is concentrated at a gentle heat, and the evaporation completed in vacuo.

Glycerin, dried in vacuo at  $212^\circ$ , is a syrupy, colourless, inodorous liquid, tasting like sugar, from which circumstance it has derived its name, (*γλυκύς*, sweet,) insoluble in water, but soluble in all proportions in alcohol and ether. It is decomposed by heat, yielding very complex products; among which is remarked an oily, colourless, extremely disagreeable-smelling liquid, called *acrolein*, and presenting the formula  $C_6H_4O_2$ . Oxidizing substances, such as ordinary nitric acid, or a mixture of sulphuric acid and peroxide of manganese, form with glycerin, oxalic, formic, and carbonic acids. Chlorine and bromine act on glycerin, and form chlorinated and brominated compounds, which can only be expressed in equivalents by doubling the ordinary formula of glycerin, that is, by writing it  $C_{12}H_{14}O_{10}, 2HO$ , which furnishes,

Original glycerin.....	$C_{12}H_{14}O_{10}, 2HO$ ,
Trichlorinated “ .....	$C_{12}H_{11}Cl_3O_{10}$ ,
Tribrominated “ .....	$C_{12}H_{11}Br_3O_{10}$ .

But it is difficult to decide the question, owing to the want of means of ascertaining the purity of the chlorinated and brominated substances, inasmuch as they do not crystallize.

By mixing 2 parts of concentrated sulphuric acid with 1 part of glycerin, combination ensues, with elevation of temperature; and by leaving the mixture to itself for some time, shaking it frequently, an acid compound, *sulphoglyceric acid*, is produced, which forms soluble salts with lime and oxide of lead; the lime-salt being prepared by adding water to the mixture, saturating it with chalk, and filtering to separate the sulphate of lime. The liquor, when evaporated, yields sulphoglycerate of lime, of which the formula, when it is dried at  $248^\circ$  in vacuo, is  $CaO(C_6H_7O_5, 2SO_3)$ , and which dissolves in one-half of its weight in water, but it is insoluble in alcohol and ether.

Glycerin also becomes heated when it is mixed with anhydrous or hydrated phosphoric acid; a *phosphoglyceric acid*, which dissolves in water, being formed. By saturating the liquid with carbonate of baryta, and lastly by caustic baryta, the free phosphoric acid is precipitated in the state of phosphate of baryta, while the liquid contains *phosphoglycerate of baryta*, which is separated by evapora-

tion. The formula of this salt, dried at  $284^{\circ}$ , is  $2\text{BaO}, (\text{C}_6\text{H}_7\text{O}_5, \text{PO}_3)$ .

Phosphoglyceric acid has been found ready formed in the yolk of eggs.

Sulphoglyceric and phosphoglyceric acids yield a large quantity of acrolein when they are decomposed by heat; which is, in fact, the best method of preparing this substance.

#### *Stearin and Stearic Acid.*

§ 1597. The most efficient method of isolating stearin consists in melting tallow with oil of terpentine, when the oil, after being decanted, deposits a solid substance on cooling, which is subjected to pressure between the folds of tissue-paper in a press. After being similarly treated several times, it is dissolved in ether, with the assistance of heat, when the greater portion of it is again deposited on cooling. The stearin thus obtained is considered as pure. Chemical analysis, added to the knowledge of its products of saponification, have assigned to stearin the formula  $\text{C}_{142}\text{H}_{140}\text{O}_{16}$ , which is more properly written  $(\text{C}_6\text{H}_7\text{O}_5 + \text{HO}), 2\text{C}_{68}\text{H}_{66}\text{O}_5$ .

Stearin is therefore admitted to be an acid compound, analogous to sulphovinic acid  $(\text{C}_4\text{H}_5\text{O}, \text{HO})2\text{SO}_3$ , and formed by the combination of 2 equiv. of stearic acid  $\text{C}_{68}\text{H}_{66}\text{O}_5$  with 1 equiv. of glycerin and 1 equiv. of water.

Stearin crystallized in ether forms small white lamellæ, of a pearly lustre, melting at from  $140^{\circ}$  to  $144^{\circ}$ , and setting, on cooling, into a white opaque mass, presenting no appearance of crystallization. It is completely insoluble in water, but dissolves in 8 parts of boiling alcohol, separating from it almost entirely on cooling; while ether dissolves a large proportion of it at the boiling point, but when cooled only retains about  $\frac{1}{20}$ .

§ 1598. *Stearic acid* is an important article of commerce, of which candles, called *stearic candles*, are made. It is prepared by saponifying beef or mutton suet by lime: 500 kilog. of suet and 800 litres of water are placed in a wooden vat, holding 2000 litres, and lined with lead, and heated by steam conveyed directly into the vat by means of a circular tube pierced with holes; and when the suet is melted, about 600 litres of a solution of lime, containing 60 kilog. of quicklime, is added, and the mixture is continually stirred. After 6 or 7 hours, the saponification is terminated, and the soap of lime has formed a consistent mass, which becomes very hard on cooling. It is reduced to a fine powder, and decomposed by sulphuric acid, diluted with water, in vats similar to the first, and heated by steam, when the fatty acids, set free, form an oily layer on the surface of the acid liquids.

The melted fat is decanted, and washed several times, while hot, with water charged with sulphuric acid, and then with fresh water; and it is finally run into tin moulds, forming cakes of 3 or 4 kilogs.

in weight. This mass, which is still a mixture of stearic, margarinic, and oleic acids, is first powerfully compressed when cold, in order to express the greater part of the oleic acid, and then at a temperature of  $90^{\circ}$  or  $100^{\circ}$ , to drive out the remainder. The oleic acid thus expressed is of a deep brown colour, and contains nearly all the margarinic, besides a certain quantity of stearic acid. The cakes remaining after this compression are again melted, in contact with a dilute solution of sulphuric acid, which removes the last traces of lime from the fatty substance; after which it is freed from the adhering acid by washing it in boiling water. It is then poured into moulds, where it becomes solid, and is thus brought into commerce as refined stearic acid, used for the manufacture of candles.

§ 1599. Large quantities of solid fat acids are now prepared for the manufacture of stearic candles by a very ingenious process, in which saponification by sulphuric acid is combined with distillation of the fat acids, in intensely heated steam, having but little tension. This process enables the use of fats of all kinds, and of the most inferior qualities.

The fats, placed in boilers heated by steam, are first treated with a quantity of concentrated sulphuric acid, which varies from 6 to 15 per cent., according to the nature of the fat. The temperature being raised to  $212^{\circ}$ , and kept at that point for 15 or 20 hours, under constant stirring, the fat acids are set free, and the glycerin is almost wholly converted into sulphoglyceric acid; while the greater portion of the foreign substances are destroyed by the sulphuric acid, yielding carbonaceous residues and products soluble in water. The fat acids are washed with water, and then placed in a distilling apparatus, through which steam heated to about  $600^{\circ}$  is passed, with an elastic force inferior to that of the atmosphere, when the fat acids distil with the water, and by pressure can be brought into a state fitted for the manufacture of candles.

§ 1600. Very pure stearic acid may be obtained, for laboratory purposes, by crystallizing the stearic acid of commerce several times in boiling alcohol.

Stearic acid yields, by slow cooling, beautiful and pearly crystals, melting at  $158^{\circ}$ , and at a temperature of  $570^{\circ}$  giving off vapour without alteration. It may be distilled in vacuo, and is completely insoluble in water, but very soluble in boiling alcohol and ether. The formula of crystallized stearic acid is  $C_{68}H_{68}O_7$ , which should be written  $C_{68}H_{66}O_5 \cdot 2HO$ , since 2 equiv. of a base may be substituted for 2 equiv. of water; showing it, therefore, to be a bibasic acid.

The acid forms two salts with potassa: *bipotassic stearate*  $2KO$ ,  $C_{68}H_{66}O_5$ , and *monopotassic stearate*  $(KO+HO)$ ,  $C_{68}H_{66}O_5$ .\* The former is obtained by treating stearic acid with an equal weight of

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\* These salts would with more propriety be called basic and neutral stearates of potassa.—W. L. F.



hydrate of potassa, dissolved in 20 parts of water, when the salt remains in the form of clots, which are compressed between tissue-paper. It is then redissolved in 15 or 20 parts of boiling alcohol, and the liquid allowed to cool, when the bipotassic stearate is deposited in white crystalline lamellæ. It dissolves without change in 10 times its weight of water, but, when cold, produces only a mucilaginous liquid, which does not become perfectly fluid and limpid unless it be heated to boiling. When a larger quantity of water is poured into this solution, a clouded, opalizing liquid is obtained, in which a large number of small crystalline spangles of extreme delicacy swim, and which settle to the bottom of the vessel, if it be allowed to rest. These small crystals constitute monopotassic stearate, of which the formula is  $(\text{KO} + \text{HO}), \text{C}_{68}\text{H}_{66}\text{O}_6$ . Alcohol does not effect this decomposition in the bipotassic stearate.

Soda forms two stearates analogous to those of potassa: stearates of baryta, strontian, and lime, which present the formula  $2\text{RO}, \text{C}_{68}\text{H}_{66}\text{O}_6$ , are prepared by double decomposition from the bipotassic stearate, and are completely insoluble in water. The lead-salt is obtained in the same way, but the stearate of lead used in pharmacy for the making of *plasters* is prepared by directly saponifying fats by litharge in the presence of water. Spring-water is generally *hard*, and is then unsuitable for washing, owing to the presence of calcareous salts, which decompose the alkaline soaps as they form, and make insoluble soaps; and alkaline soap can only dissolve when the calcareous salts are completely decomposed. Water is rendered fit for washing by adding a small quantity of carbonate of soda, which decomposes the salts of lime.

Stearic acid forms *vinostearic* and *methylostearic ethers*, which are obtained by dissolving stearic acid in absolute alcohol or wood-spirit, and passing through it a current of chlorohydric acid gas; when the ethers, after being precipitated by water and crystallized in alcohol, form white substances of a greasy lustre, and melting at from  $86^\circ$  to  $95^\circ$ .

#### *Margaric Acid* $\text{C}_{68}\text{H}_{66}\text{O}_6, 2\text{HO}$ .

§ 1601. By decomposing with acids a soap made of human fat, a mixture of fatty acids is obtained, melting at about  $135^\circ$ , and which is considered as composed solely of margaric and oleic acids. Margaric acid is supposed to be produced by the saponification of a simple fat, margarin, but which probably exists in combination with olein. Margaric acid is also formed in the distillation of stearic acid and the fats in general, as well as when the latter are subjected to the action of oxidizing reagents. Chemists are not agreed upon the formula of margaric acid; and while some write it  $\text{C}_{68}\text{H}_{66}\text{O}_6, 2\text{HO}$ , a formula which differs from that of stearic acid by 1 equivalent of oxygen, others assert that its composition is identical with that of stearic acid.

The best method of preparing margaric acid consists in saponifying human fat or olive-oil by potassa, and pouring acetate of lead into the solution, which yields a precipitate of margarate and oleate of lead. The precipitate being treated several times with ether, which completely dissolves the oleate of lead, and a much smaller proportion of margarate, the remaining margarate of lead is decomposed by dilute nitric acid, and the margaric acid arising from it is purified by crystallization in alcohol. In its physical properties, margaric closely resembles stearic acid, but it melts at a lower temperature, viz. at  $140^{\circ}$ . It forms two salts with potassa: the *bipotassic margarate*  $2\text{KO}, \text{C}_{68}\text{H}_{66}\text{O}_6$ , and the *monopotassic margarate*  $(\text{KO} + \text{HO}), \text{C}_{68}\text{H}_{66}\text{O}_6$ ; which are formed under the same circumstances as the corresponding stearates, and nearly resemble them.

*Oleic Acid*  $\text{C}_{36}\text{H}_{33}\text{O}_3, \text{HO}$ .

§ 1602. In order to separate this acid, oils very rich in olein, such as olive-oil and oil of almonds, are saponified by potassa; when the soap is decomposed by tartaric acid, and the fatty acids which separate are decanted. The latter are digested in a water-bath with one-half of their weight of finely-powdered oxide of lead, thus forming a soap of lead, consisting of both the oleate and the margarate. This soap is digested for 24 hours with twice its volume of ether, which dissolves the oleate, and the ethereal liquor being evaporated, the oleate of lead is decomposed by chlorohydric acid. The oleic acid thus obtained is, however, not pure, and must be redissolved in ammonia, precipitated by chloride of barium, and the oleate of baryta must be purified by several crystallizations in boiling alcohol. Lastly, the oleate of baryta is decomposed by tartaric acid, operating in a bottle perfectly fitted and well corked, to prevent the oleic acid from absorbing the oxygen of the air.

Oleic acid is a colourless liquid, solidifying below  $53.6^{\circ}$ , and insoluble in water, but very soluble in alcohol, ether, and the essential oils. It does not redden litmus, even when dissolved in alcohol; and it readily absorbs oxygen from the air. The formula  $\text{C}_{36}\text{H}_{33}\text{O}_3, \text{HO}$ , which has generally been assigned to this acid, should probably be doubled and written  $\text{C}_{72}\text{H}_{66}\text{O}_6, 2\text{HO}$ , in which latter case the acid would be considered as bibasic. Oleic acid is decomposed by heat, but may nevertheless be distilled in vacuo. The products of its decomposition are very various; and a fatty acid, called *sebacic*, which characterizes oleic acid under these circumstances, is remarked among them. Treated with nitrous acid, oleic acid is easily transformed into an isomeric modification, *elaidic acid*, which sets into a crystalline mass, and which shows a very strong acid reaction. It dissolves in boiling alcohol, and separates partly from it, on cooling, in large crystalline lamellæ, which melt only at  $111.2^{\circ}$ .  $\frac{1}{260}$  of nitrous acid will effect the transformation of oleic acid, but it rapidly increases with the quantity of nitrous acid used. Elaidic acid

oxidizes rapidly in the air, particularly if it be heated to  $140^{\circ}$  or  $160^{\circ}$ .

The alkaline oleates are readily formed by dissolving oleic acid in alkaline lixivæ, or by treating the alkaline carbonates by an alcoholic solution of oleic acid; other metallic oleates being prepared by double decomposition. The formula of oleate of baryta is  $\text{BaO}$ ,  $\text{C}_{35}\text{H}_{33}\text{O}_2$ . A large quantity of water decomposes the alkaline oleates, salts containing a smaller proportion of base being deposited; which decomposition is however less readily effected than in the stearates and margarates.

#### ACTION OF SULPHURIC ACID ON THE NATURAL FATS.

§ 1603. When sulphuric acid is made to act on stearin, the latter is decomposed in the same manner as when in contact with the hydrated alkalies; stearic acid being set free, and the glycerin combining with the sulphuric acid to form sulphoglyceric acid. It is as yet unknown what reaction sulphuric acid exerts on margarin or on olein when isolated; the reaction on the natural fats, which are mixtures or compounds of these two substances, and particularly on olive-oil, having hitherto only been studied.

When olive-oil is treated with one-half of its weight of concentrated sulphuric acid, by placing the bottle containing the two substances in a refrigerating mixture, in order to prevent an elevation of temperature, a homogeneous liquid of a viscous consistence is formed, composed of sulphoglyceric acid and two new compound acids, called *sulphomargaric* and *sulpholeic*. By adding a great excess of cold sulphuric acid, the sulphomargaric and sulpholeic acids are separated from the sulphoglyceric acid, which remains in solution, while they form an oily coating on the surface, which is removed and washed with a small quantity of water, to free it from the sulphuric acid. These acids dissolve readily in water and alcohol, and form well-defined salts. Their aqueous solution decomposes spontaneously in the cold, and more rapidly at the boiling point, into sulphuric acid, and new fat acids, which appear to differ from margaric and oleic acids only by the addition of 1 or more equivalents of water. Margarin yields the three acids, *metamargaric*, *hydromargaric*, and *hydromargaritic*; while oleic acid furnishes but two, *metoleic* and *hydroleic acids*. The three acids derived from margarin are solid at the ordinary temperature, metamargaric acid melting at  $122^{\circ}$ , hydromargaric at  $140^{\circ}$ , and hydromargaritic at  $154^{\circ}$ ; while metoleic and hydroleic acids are oily liquids. All the new fat acids, being insoluble in water, are readily soluble in alcohol and ether.

Metoleic and hydroleic acids, carefully heated in a retort, are decomposed, and disengage pure carbonic acid, while, together with some empyreumatic substances, an oily liquid, composed of two isomeric carburetted hydrogens, presenting the composition of olefiant

gas, condense in the receiver, and may be separated by distillation at different temperatures. The first, *oleen*, boils at  $131^{\circ}$ , has a disagreeable and penetrating odour, and the density of its vapour has been found to be 2.87, while its formula is  $C_{12}H_{12}$ , which is represented by 4 volumes of vapour. The second compound, *elaen*, the formula of which appears to be  $C_{18}H_{18}$ , boils at  $230^{\circ}$ .

#### ACTION OF NITRIC ACID ON STEARIC, MARGARIC, AND OLEIC ACIDS.

§ 1604. Nitric acid reacts energetically on the fat acids, forming with them very complicated products, among which are some new and highly interesting acids. Since during the first periods of the reaction of nitric on stearic acid the latter is converted into margaric acid, the products afforded by margaric and oleic acids only remain to be described. The ultimate products of the reaction are very complicated, and may be divided into two classes: the volatile acids which condense in the receiver, and the fixed or slightly volatile acids which remain in the retort. We shall here enumerate them with their formula, in order that the curious relation between them may be more easily seen. The fourth column contains the carburetted hydrogens from which they may be supposed to be derived by substitution.

Volatile Acids.			
Formic	acid	..... $C_2H_2O_4$ or $C_2H_3O_3,HO$	..... $C_2H_4$
Acetic	"	..... $C_4H_4O_4$	$C_4H_3O_3,HO$ ..... $C_4H_6$
Acetonic	"	..... $C_6H_6O_4$	$C_6H_5O_3,HO$ ..... $C_6H_8$
Butyric	"	..... $C_8H_8O_4$	$C_8H_7O_3,HO$ ..... $C_8H_{10}$
Valerianic	"	..... $C_{10}H_{10}O_4$	$C_{10}H_9O_3,HO$ ..... $C_{10}H_{12}$
Caproic	"	..... $C_{12}H_{12}O_4$	$C_{12}H_{11}O_3,HO$ ..... $C_{12}H_{14}$
Ænanthyllic	"	..... $C_{14}H_{14}O_4$	$C_{14}H_{13}O_3,HO$ ..... $C_{14}H_{16}$
Caprylic	"	..... $C_{16}H_{16}O_4$	$C_{16}H_{15}O_3,HO$ ..... $C_{16}H_{18}$
Pelargonic	"	..... $C_{18}H_{18}O_4$	$C_{18}H_{17}O_3,HO$ ..... $C_{18}H_{20}$
Capric	"	..... $C_{20}H_{20}O_4$	$C_{20}H_{19}O_3,HO$ ..... $C_{20}H_{22}$

It will be seen that if the equivalent of basic water be not separated in the formula, all these acids may be regarded as compounds of 4 equivalents of oxygen with carburetted hydrogen isomeric with olefant gas. If, on the contrary, the basic water be isolated, they may be regarded as resulting from the substitution of 3 equivalents of oxygen for 3 equivalents of hydrogen in carburetted hydrogens of which the general formula is  $C_{2n}H_{2n+2}$  ( $n$  being a whole number :) but only one of these carburetted hydrogens, the protocarburetted  $C_2H_4$ , is as yet known with certainty.\*

\* This theory has already been noticed in the note to § 1401, where it is also shown that the acids in the above table may more properly be considered as oxalic acid paired with one equiv. of a carburetted hydrogen of the general

The slightly volatile acids which remain in the retort are

Succinic acid	.....	$C_8H_6O_8$	or	$C_8H_4O_6, 2HO$
Adipic	“	.....	$C_{12}H_{10}O_8$	$C_{12}H_8O_6, 2HO$
Pimelic	“	.....	$C_{14}H_{12}O_8$	$C_{14}H_{10}O_6, 2HO$
Suberic	“	.....	$C_{16}H_{14}O_8$	$C_{16}H_{12}O_6, 2HO$
Sebacic	“	.....	$C_{20}H_{18}O_8$	$C_{20}H_{16}O_6, 2HO$

If we omit the basic water contained in the formula, we shall find all these acids to result from the combination of 8 equivalents of oxygen with the carburetted hydrogens of which the general formula is  $C_{2n}H_{2(n-1)}$ .

§ 1605. In order to obtain these various products, it is necessary to operate on a somewhat considerable quantity of oleic acid. The nitric acid should be first introduced by itself into a tubulated retort, and heated to  $120^\circ$  or  $140^\circ$ , the oleic acid being added by small quantities at a time. Violent reaction ensues at each addition; and when all the oleic acid has been poured into the retort, the heat is continued until reaction ceases. The liquid collected in the receiver consists of water containing the most soluble of the volatile acids, such as formic, acetic, acetic, and butyric acids, covered by an oily layer which contains the valerianic and other acids. The latter is decanted, saturated with water of baryta, and the various salts of baryta formed are separated by successive crystallizations. The caproate of baryta crystallizes first, and then successively the oenanthylate, the caprylate, the pelargonate, the caprate, and lastly the valerianate of baryta.

The more volatile acids, when dissolved in water, are saturated by carbonate of soda, and the solution evaporated; when the first crystals deposited from the cold solution are acetate of soda; while if sulphuric acid be then poured into the mother liquid, an oily layer, composed of butyric and metacetic acids, is separated.

When the slightly volatile acids which remain in the retort are chiefly sought to be obtained, the action of the nitric acid must not be too much prolonged, since a portion of them would then be destroyed. The oleic acid is then acted on by double its weight of nitric acid, and the action is continued until no more reddish vapours are disengaged, when a portion of the oleic acid has disappeared, being converted into products which dissolve in the aqueous liquid. The supernatant oil is decanted, and again acted on by nitric acid; this process being continued until it has nearly disappeared, when the slightly volatile acids are found in the watery liquids arising from this treatment.

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formula  $C_{2n}H_{2n+1}$ . The substitution of oxygen for hydrogen is in no case admissible; and while of the hydrocarbons assumed in the text as the radicals only one is known, several of the formula just mentioned have been isolated, such as methyl  $C_2H_5$ , ethyl  $C_4H_9$ , valyl  $C_5H_9$ , and amyl  $C_{10}H_{21}$ .—*W. L. F.*

*Succinic Acid*  $C_4H_4O_6 \cdot 2HO$ .

§ 1606. Succinic acid is produced not only by the action of nitric acid on fatty acids, but is also found under other remarkable circumstances. It is generally prepared by distilling *amber*, a substance of organic origin, sometimes found in strata of lignite, and occurring in large quantities in the alluvial sands of the Baltic. Amber distilled in a glass retort yields an acid water, and empyreumatic oils, which remain in the paper through which the acid liquid is filtered. The latter being saturated with chlorine in order to destroy some foreign substances, and then evaporated, the succinic acid is deposited in crystals.

An aqueous solution of impure asparagin left to itself for some time is converted by a species of fermentation into succinate of ammonia. Impure neutral malate of lime, such as is directly obtained from the berries of the service-tree, left for several months, under a layer of water, in a vessel covered merely by a sheet of paper, undergoes an analogous fermentation, the liquor becoming covered with mucilage, while crystals of hydrated carbonate of lime are deposited on the sides of the vessel, and acicular crystals of succinic acid are developed on the deposit of malate of lime.

Succinic acid melts at  $365^\circ$ , boils without alteration at  $473^\circ$ , and may be sublimed at much lower temperatures. Cold water dissolves about  $\frac{1}{5}$  of its weight of it, and boiling water about  $\frac{1}{2}$ ; and it also dissolves in considerable quantity in alcohol, but very slightly in ether. The formula of succinic acid, crystallized in water, is  $C_4H_4O_6$ , which is generally written  $C_4H_4O_6 \cdot 2HO$ , since 2 equiv. of base may be substituted for 2 equiv. of water. At  $284^\circ$  it loses 1 equiv. of water, and after several distillations becomes perfectly anhydrous; its composition then corresponding to the formula  $C_4H_4O_6$ .

Nitric acid and chlorine do not sensibly act on succinic acid, while anhydrous sulphuric acid forms a compound acid with it, called *sulphosuccinic*.

*Adipic Acid*  $C_{12}H_{10}O_8 \cdot 2HO$ .

§ 1607. This acid is formed by the reaction of nitric on oleic acid, being deposited after the suberic and pimelic acids, which are less soluble. The best method of preparing it consists in boiling, in a large retort furnished with its receiver, tallow with nitric acid of commerce, renewed until the fatty substance has entirely disappeared. The distilled portions are returned to the retort, and the reaction of the nitric acid is continued until crystals appear in the receiver, after which the liquid is concentrated in a water-bath, when it coagulates into a crystalline mass. It is washed, first with concentrated nitric acid, then with the same acid more diluted, and lastly with fresh water. Treated again with boiling water, it dissolves and deposits, on cooling, very pure crystals of adipic acid.

VOL. II.—3 I

This acid melts at  $266^{\circ}$ , may be distilled without alteration, and forms well-marked salts, of which the general formula is  $2RO, C_{12}H_8O_6$ . When an alcoholic solution of adipic acid is saturated with chlorohydric acid gas, an oil is obtained having the smell of pippin apples, and known by the name of *adipic ether*  $2C_4H_5O, C_{12}H_8O_6$ .

*Suberic Acid*  $C_{16}H_{12}O_6, 2HO$ .

§ 1608. Suberic acid is formed by the action of nitric acid on fats, being the first deposited when the liquid is crystallized; while it has also been directly obtained by causing the same acid to act on cork, which is the most convenient method of preparing it. The rasped cork being boiled with nitric acid of commerce, the acid liquid is concentrated by distillation, and allowed to cool, when suberic acid is deposited, and may be purified by solution in boiling water and recrystallization.

Suberic acid forms small, hard, granular crystals, soluble in about 2 parts of boiling water, which scarcely retains  $\frac{1}{100}$  after cooling, while it is very soluble in alcohol and ether, especially at the boiling point. The alkaline suberates are soluble in water, and nitrate of silver effects in their solution a precipitate of suberate of silver, of the formula  $2AgO, C_{16}H_{12}O_6$ .

By saturating an alcoholic solution of suberic acid with chlorohydric acid gas, *vinosuberic ether*  $2C_4H_5O, C_{16}H_{12}O_6$  is obtained, as an oleaginous, colourless liquid, which boils at about  $500^{\circ}$ .

*Sebacic Acid*  $C_{20}H_{16}O_6, 2HO$ .

§ 1609. It has been mentioned (§ 1602) that sebacic acid is constantly formed in the distillation of substances containing olein or oleic acid, and that it is regarded as characteristic of these substances: it is separated by treating the distilled products several times with boiling water. Acetate of lead is poured into the solution, and the salt of lead precipitated is decomposed by sulphuric acid, when the sebacic acid is deposited from the boiling aqueous solution in the form of crystalline, pearly lamellæ. This acid melts at  $260.6^{\circ}$ , distils without alteration, and is slightly soluble in cold, but much more freely in boiling water, while alcohol and ether dissolve it readily. It forms crystallizable salts with the alkalies of the general formula  $2RO, C_{20}H_{16}O_6$ . It produces a compound ether  $2C_4H_5O, C_{20}H_{16}O_6$  under the same circumstances as the preceding acids.\*

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\* The admirable examination of the fats and fat acids by *Chevrel* was the first investigation which gave an insight into the chemistry of organic compounds. But more recent investigations have developed the singular transformations to which they are subject; such as, the action of sulphuric acid, their oxidation into other acids, &c.—*W. L. F.*

## OF SOME VOLATILE ACIDS EXTRACTED FROM NATURAL FATS.

*Hircic Acid.*

§ 1610. Hircic acid is obtained by saponifying the fat of the goat by an alkali, and decomposing the soap resulting by tartaric acid; after which the aqueous liquid is separated and distilled, when the hircic acid, being volatile, passes into the receiver. It is saturated with water of baryta, and the hircate of baryta, which is obtained by evaporation, is decomposed by distilling it with sulphuric acid diluted with its weight of water, when the hircic acid forms an oily stratum on the surface of the water which condenses in the receiver. It has a decided goatlike smell, is slightly soluble in water, but easily so in alcohol or ether, and its composition is unknown.

*Phocenic Acid.*

§ 1611. The oil of the sperm whale and dolphin yields, by saponification, in addition to the ordinary fat acids, a peculiar volatile acid, called *phocenic*, which appears to be identical with valerianic acid.

*Caproic, Capric, and Caprylic Acids.*

§ 1612. These three acids are found among the products of the oxidation of oleic by nitric acid, and are also obtained mixed with butyric acid when butter is saponified by the alkalies. It is admitted that butyric, capric, caproic, and caprylic acid in butter are combined with glycerin, and form peculiar substances: butyrin, caprin, caproin, and caprylin.

In order to prepare these substances, butter is kept for a long time at a temperature approaching its melting point, when a liquid portion separates, in which the butyrin, caprin, caproin, and caprylin are principally concentrated. This oily portion is treated, after being decanted, with an equal part of anhydrous alcohol, and shaken frequently; the alcoholic solution leaving by evaporation an oil formed of a mixture of butyrin, caprin, caproin, and caprylin.

If, on the contrary, the butyric, capric, and caproic acids are to be isolated, the butter is saponified with an alkali, and the soap decomposed by an aqueous solution of tartaric acid, when the acids sought remain in the watery liquid; which is separated and distilled. The acids, being volatile, pass over, and are then saturated with caustic baryta, and evaporated, which furnishes a mixture of butyrate, caprate, caprylate, and caproate of baryta. The salts are separated by crystallization, the caprate of baryta being first deposited, then the caprylate, the caproate, and lastly the butyrate. The acid of each of these salts may be easily separated by distilling them with a small excess of sulphuric acid diluted with its



weight of water, when the acid passes into the receiver with the water, and forms an oily coating on its surface.

*Capric acid* is liquid above  $62.6^{\circ}$ , but solidifies into crystalline aciculæ when the temperature is lower; and it is very slightly soluble in water, but readily so in alcohol. The formula of free capric acid is  $C_{20}H_{40}O_2$ , that of the caprates being  $RO, C_{20}H_{39}O_2$ .

*Caprylic acid* is solid below  $57.2^{\circ}$ , and boils at about  $464^{\circ}$ . Water dissolves only a very small quantity of it, even at the boiling point, while it is very soluble in alcohol and ether; and the general formula of the caprylates is  $RO, C_{16}H_{31}O_2$ .

*Caproic acid* is an oily liquid at the ordinary temperature, and does not solidify even at  $14^{\circ}$ , while it boils at about  $410^{\circ}$ , and dissolves in 75 parts of water and in all proportions in alcohol. The general formula of its salts is  $RO, C_{12}H_{23}O_2$ .

These various acids form compound vinic and methylic ethers, which may be obtained by passing chlorohydric acid gas through alcohol or wood-spirit holding the acids in solution.

#### PALM-OIL.

§ 1613. This oil, which is imported chiefly from Guinea, has, of late years, become an object of great commercial importance. It is generally of a reddish-yellow colour, and melts at a temperature varying from  $80^{\circ}$  to  $86^{\circ}$ . It is supposed to be formed of olein, margarin, and a new fatty substance, called *palmitin*, which is extracted by expressing the oil and washing the residue several times with alcohol, when the palmitin is isolated and purified by being washed in ether. Palmitin forms crystalline aciculæ, melting at  $118.4^{\circ}$ , but decomposing at a high temperature; and it is nearly insoluble in alcohol, even at the boiling point, but dissolves largely in ether. Alkalies convert it into glycerin, and into a new acid called *palmitic*. Its composition corresponds to the formula  $C_{70}H_{140}O_2$ , which is written  $C_6H_4O_2, C_{64}H_{136}O_2$ ; the formula of free palmitic acid being  $C_{64}H_{128}O_2, 2HO$ .

#### CASTOR-OIL.

§ 1614. Castor-oil is extracted from the *ricinus communis*, and forms a white or somewhat yellowish oil, slightly fluid, which soon becomes rancid in the air. When saponified, it yields glycerin, and three new fatty acids: *stearoricinic*, called also *margaritic*, *ricinic*, and *oleoricinic* or *elaiodidic acids*. By decomposing, by an acid, soap made with castor-oil, an oil separates, which partially coagulates at the ordinary temperature. The solid part being separated and expressed between bibulous paper, the residue is dissolved in boiling alcohol, when, on cooling, pearly crystalline lamellæ of stearoricinic acid separate, which melt only at  $266^{\circ}$ . The greater portion of the oil which has been separated by expression from the stearoricinic acid coagulates at  $28.4^{\circ}$ , and is also separated, by expression

between tissue-paper, from the portion which remains liquid, when it constitutes ricinic acid, which melts at  $71.6^{\circ}$ , and may be distilled without alteration. Lastly, the name of *oleoricinic acid* has been given to the portion of the acid oil which did not become solid at  $28.4^{\circ}$ .

## SPERMACETI.

§ 1615. A peculiar fat oil, which, by exposure to the air for a few days, deposits a crystalline substance called *spermaceti*, is extracted from the brain of the sperm whale. The crystalline mass is expressed to separate the part which remains liquid, and digested in a hot lye of potassa, while the oily fluid is washed several times with boiling water, and poured into crystallizing vessels, in which it solidifies into crystalline masses, constituting the cakes of spermaceti found in commerce. In order to obtain it in a state of purity, it is necessary to crystallize it several times in alcohol, when it takes the name of *cetin*.

Cetin is a white substance of a crystalline texture, almost inodorous, melting at  $120.2^{\circ}$ , and solidifying, by slow cooling, into a mass composed of large crystalline lamellæ. It is insoluble in water, and 100 parts of boiling alcohol dissolve 16 parts of it, but retain only 3 after cooling; while ether and the essential oils dissolve it freely. Its composition corresponds to the formula  $C_{32}H_{32}O_2$ . Spermaceti is saponified by potassa, but it differs from all fat substances we have hitherto described by yielding no glycerin, but in its place another very remarkable neutral substance, called *ethal*, while the fat acid which combines with the alkali has received the name of *ethalic acid*. The saponification of spermaceti is much more difficult than that of the other fats, since it can only be effected by a concentrated solution of potassa, assisted by heat, and continued for several days; or better, by melting 2 parts of spermaceti in a capsule and adding 1 part of caustic potassa broken into small pieces, and stirring it constantly. After some time, as soon as the substance has become completely solid, it is treated with boiling water and chlorohydric acid, when the ethalic acid separates and forms an oily layer on the surface of the liquid. The oil being decanted, and treated in the same manner by potassa, is again saturated with chlorohydric acid, and the oil obtained is heated with hydrated lime, when the ethalic acid alone combines with the lime, leaving the ethal isolated. The latter is removed by boiling alcohol, which is then driven off by distillation, and it is finally crystallized by dissolving it in ether.

Ethal melts at  $118.4^{\circ}$ , crystallizing readily, on cooling, in brilliant lamellæ, and it is insoluble in water, but dissolves in all proportions in alcohol and ether. It may be distilled without alteration. Its composition corresponds to the formula  $C_{32}H_{34}O_2$ , and exhibits several reactions which assimilate it to alcohol and wood-spirit, on which account it has even been called *ethalic alcohol*.

§ 1616. If a mixture of ethal and concentrated sulphuric acid be heated, stirring it frequently, an acid product is obtained consisting of a mixture of pure sulphuric acid and a compound acid, *sulph-ethalic acid*  $(C_{32}H_{33}O + HO), 2SO_3$ , which is to ethal  $C_{32}H_{34}O_2$  what sulphovinic acid  $(C_4H_5O + HO), 2SO_3$  is to alcohol  $C_4H_6O_2$ . The acid mass being dissolved in alcohol and saturated with potassa, sulphate of potassa is precipitated, while the sulphethalate of potassa  $(C_{32}H_{33}O + HO), 2SO_3$  remains in solution, and crystallizes by evaporating the liquid.

By heating in a retort equal volumes of ethal and perchloride of phosphorus, chlorohydric acid is disengaged, and protochloride of phosphorus first distils, then the perchloride, and lastly an oily product of the composition  $C_{32}H_{33}Cl$ , which may be regarded as the *chlorohydric ether* of ethalic alcohol  $C_{32}H_{34}O_2$ . In order to obtain it pure, it should be distilled a second time with perchloride of phosphorus, washed with water, and distilled over a small quantity of quicklime.

By heating ethal with 5 or 6 times its weight of potassic lime to a temperature of  $410^\circ$  to  $430^\circ$ , pure hydrogen is disengaged, and ethalic acid  $C_{32}H_{33}O_3, HO$  is formed, which is to ethalic alcohol  $C_{32}H_{34}O_2$  what acetic acid  $C_4H_3O_3, HO$  is to vinic alcohol  $C_4H_6O_2$ . In order to separate this acid, the alkaline mass is diluted with water and saturated with chlorohydric acid, when the ethalic acid separates in the form of flocculi, but always mixed with unaltered ethal. In order to purify it, it is heated with a solution of caustic baryta, which combines with the ethalic acid, after which it is evaporated to dryness, and the residue treated with alcohol to dissolve the ethal. The residue, which is composed only of ethalate of baryta, is decomposed by chlorohydric acid, while the ethalic acid, set free, is purified by solution in ether.

§ 1617. We have shown (§ 1615) that spermaceti is converted by saponification into ethal and ethalic acid; and a large quantity of the latter acid may also be obtained by decomposing spermaceti soaps by acids.

Ethalic acid melts at about  $140^\circ$ , crystallizing, on cooling, in brilliant aciculæ; and it is insoluble in water, but very soluble in alcohol and ether. The general formula of its salts is  $RO, (C_{32}H_{31}O_3)$ .

As ethalic acid exists in palm-oil, either isolated or combined with glycerin, it has also received the name of *palmitic acid*.

By distilling ethal several times with anhydrous phosphoric acid, a volatile liquid of the formula  $C_{32}H_{32}$  is obtained, which has been called *ceten*, and forms in the series of ethalic alcohol the analogue of olefiant gas in the vinic series. This liquid boils at about  $527^\circ$  without alteration, and its formula corresponds to 4 volumes of vapour.

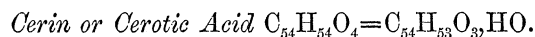
## WAX.

§1618. Chemists give the name of *wax* to substances arising from various sources, the type of which, beeswax, will alone occupy our attention, because it is best known; and we shall omit the other substances produced by vegetables, which frequently resemble ordinary wax only in appearance or in physical properties.

Wax forms the solid portions of the honeycomb; and when the honey has been removed by expression, the wax is melted with hot water, and washed several times with water, when a yellow substance remains, the smell of which resembles that of honey. By exposing it in large sheets on the grass to the action of moist air and the rays of the sun, the odoriferous and colouring substances are destroyed, and white wax remains; the bleaching being more promptly effected by chlorine or the alkaline hypochlorites, and by oxidizing reagents in general. White wax contains less carbon and more oxygen than yellow wax.

Bleached wax is translucent to a certain degree, shows a density varying from 0.960 to 0.996, is hard and brittle at 32°, but very malleable at 86°, and melts at about 149°. Boiling alcohol separates it into, (1) *myricin*, almost insoluble in boiling alcohol; (2) *cerin*, also called *cerotic acid*, soluble in boiling alcohol, but deposited from it, on cooling, in small crystalline aciculæ; and (3) into *cerolein*, which remains in solution in the alcohol when cooled. The proportions of these substances vary.

Wax yields, by distillation, a small quantity of acid water, combustible gases, and liquid oils, isomeric with olefiant gas, besides a solid substance, composed essentially of margaric acid and a crystallizable substance very analogous to paraffin. By distilling it with lime, yellow oils of complex composition are first obtained, and then a large quantity of the crystalline substance about to be described.



§1619. When wax is boiled for some time with alcohol, and the liquor allowed to cool, the deposit which is formed is composed chiefly of cerin and myricin, which must be again dissolved in boiling alcohol, until the substance deposited during the cooling of the liquid melts only at 158°. It is redissolved in boiling alcohol, and acetate of lead is added, the precipitate of cerotate of lead being washed, when hot, with alcohol and ether, and then decomposed by acetic acid. The cerotic acid is crystallized by dissolving it in boiling alcohol; and the pure acid, which melts at 172.4°, is insoluble in water.

*Myricin.*

§1620. Myricin is very slightly soluble in alcohol, 200 parts of boiling alcohol being required to dissolve 1 of it, which is again

deposited, during the cooling, in white flakes; while it requires about 100 parts of cold ether for solution. It melts at  $161.6^{\circ}$ , and partly sublimes without change at a higher temperature. Its elementary composition corresponds to the formula  $C_{82}H_{92}O_4$ ; and when heated for a long time with a concentrated solution of caustic potassa, it is converted into *palmitic acid*  $C_{32}H_{31}O_3$ , HO, which remains combined with the potassa, and a neutral substance, *melissin*  $C_{60}H_{62}O_{27}$ , which in its chemical reactions resembles ethal.

*Cerolein.*

§ 1621. Cerolein, which remains in solution in the cold alcoholic liquor with which wax has been treated, is separated by evaporation from alcohol, and appears as a soft substance, fusible at  $84.2^{\circ}$ , very soluble in alcohol and cold ether, and reddening litmus. It contains more oxygen than cerin and myricin.

## ORGANIC COLOURING MATTERS.

§ 1622. While vegetables contain very various colouring matters, unequally distributed through their various parts, they also frequently enclose substances which are colourless, or nearly so, constituting a part of the living vegetable, but which acquire very beautiful colours by contact with atmospheric air or the reaction of various chemical agents.

Nearly all organic colouring matters change in the air, especially when exposed to the sun, and undergo partial combustion, being converted into colourless substances; and the quality of the colouring matter depends upon the time in which this change is effected. Chemical agents generally modify the shade of organic colouring matters, forming compounds with them or converting them into other substances equally coloured, which properties are frequently applied in dyeing. The metallic oxides especially combine with a great number of colouring matters possessing acid properties; and the majority of the oxides, such as that of alumina, tin, etc., thus form insoluble compounds, exhibiting often very beautiful colours, and which are used, under the name of *lakes*, for painting in oil and in water-colours.

Very porous charcoal, particularly animal black, absorbs the majority of organic colouring matters dissolved in water, without alteration, and again deposits them if a small quantity of alkali be added to the water; woody and animal fibre possessing the same property. Moist chlorine destroys all organic colouring matters, by exerting on them a powerful oxidizing action, owing to the decomposition of water; and sulphurous acid also bleaches them,

either by removing their oxygen, or by combining with the substance without altering it, and thus forming colourless compounds.

A large number of reducing substances, such as nascent hydrogen, sulphydric acid, the alkaline sulphides, the hydrated protoxides of iron and manganese, etc., bleach colouring matters by abstracting their oxygen.

We shall here treat only of the organic colouring matters used in dyeing.

#### COLOURING MATTERS OF MADDER.

§ 1623. Madder, (*rubia tinctorum*,) also known by the name of *alizari*, is one of the most important dyestuffs, which is extensively cultivated in the Levant and the East Indies, as well as in France, particularly in Alsace and the county of Avignon. Madder contains several colouring matters, the majority of which are as yet but imperfectly known; and the plant, while growing, contains only a yellow sap, without any red-colouring principle, the same being true of the root; while, when the latter has been separated from the plant and dried in the air, a red substance is developed which imparts its colour to all the ligneous portions.

In dyeing, sometimes crude madder is used, and sometimes that which has undergone several preparations, of which the intention is to reduce the colouring matter to a smaller volume, or to destroy some of the colouring principles, the presence of which affect the shade of the red colour.

When ground madder is exhausted by cold water, a yellow colouring matter, or *xanthin*, very soluble in water, is extracted from it; and if the residue be treated with one-half of its weight of concentrated sulphuric acid heated to  $212^{\circ}$ , a large portion of the ligneous matter is altered, becoming soluble in water, and, after several washings, yielding a brown substance, easily pulverized after desiccation, and constituting the article known in commerce by the name of *garancin* or *madder-red*. Madder-red contains another colouring matter of a beautiful red hue, called *alizarin*, mixed with some other colouring principles. When treated with boiling alcohol, it furnishes a beautifully red solution, which deposits, on evaporation, a substance of an ochrous yellow colour, and named *colorin*. Colorin is chiefly formed of alizarin, fatty matters, and a small quantity of other colouring matters; and if it be carefully heated, it emits yellow vapours, which condense in the form of bright-red needles, constituting alizarin, mixed merely with a small quantity of empyreumatic oil, from which it may easily be freed by crystallizing it in weak alcohol.

Alizarin presents all the characters of a definite compound, and its analysis has led to the formula  $C_{30}H_8O_4$ . It forms very fine aciculæ of an orange-yellow colour, nearly insoluble in cold water, slightly soluble in boiling water, but very soluble in alcohol. It

dissolves readily in alkaline lixiviæ and ammonia, furnishing solutions of a violet colour, and yielding bluish precipitates with solutions of baryta, strontian, and lime: concentrated sulphuric acid also dissolves it, forming a brown liquid, from which the alizarin is precipitated unchanged upon the addition of water.

§ 1624. Very variously coloured products have been obtained by different methods of treating madder-root, which, however, do not exhibit the characters of definite substances, and are probably only mixtures. When madder-root, previously washed, is boiled with a concentrated solution of alum, a red liquid is obtained, depositing, on cooling, a brownish-red substance, which is separated, while the filtered liquid is of a pure red, and by the addition of sulphuric acid gradually deposits the colouring matter, a mere trace of it remaining in the solution after 24 hours. The precipitate, after being washed, first with weak boiling chlorohydric acid, and then with cold water, is redissolved in alcohol, which solution is evaporated, and the residue treated several times with ether, when a colouring matter dissolves, called *purpurin* or *madder-purple*, which remains after the evaporation of the ether, in the form of a bright-red powder. This substance is insoluble in cold water, but very soluble in boiling water, alcohol, and ether; and its analysis has led to the formula  $C_{28}H_{10}O_{15}$ : but as it has not been obtained in a crystallized form, it is difficult to assert that it is a simple substance.

The name of *madder-red* is given to a colouring matter found in the brown precipitate deposited by a hot decoction of madder, on cooling; which substance sublimes at about  $437^{\circ}$ , forming crystals of a yellowish red colour, and of a composition corresponding to the formula  $C_{20}H_{10}O_{15}$ .

By dissolving the colouring matters of madder in a solution of alum, and then adding carbonate of soda, precipitates of very beautiful colour and great stability are obtained, consisting of compounds of alumina with the colouring matters, and called *madder-lakes*, which are used in painting.

#### COLOURING MATTERS OF LOGWOOD.

§ 1625. The name of *hematin* has been given to the substance to which logwood owes its value as a dyestuff. It is readily obtained by making a decoction of powdered logwood, evaporating it to dryness, and treating the residue with alcohol, when hematin is deposited in crystals, varying in depth of colour according to their size, but producing a yellow powder. The aqueous solution of hematin is colourless in the air, but if ammonia be added, it assumes an intense red hue; the substance produced by this reaction being named *hematein*, which is granular and crystalline, showing a violet-black colour and metallic lustre. It dissolves in water, and turns it of a deep purple colour. Hematein appears to differ from hematin by containing 1 equiv. less of water, the formula of dried

hematin being  $C_{16}H_7O_6, HO$ , and that of hematein  $C_{16}H_6O_6$ ; while the formula of hematin crystallized from an aqueous solution is  $C_{16}H_7O_6, HO + 2HO$ .

Hematin possesses the properties of a feeble acid, its aqueous solution being precipitated by baryta and acetate of lead. Hemate of lead, decomposed by aqueous sulfhydryc acid, forms a liquid which deposits nearly colourless crystals of hematin on evaporation.

#### COLOURING MATTERS OF SAFFLOWER.

§ 1626. The safflower is used in dyeing, and produces colours which vary from a delicate rose to a deep poppy hue. Several colouring matters exist in the flowers; and when they are exhausted by water, they yield a yellow colouring matter, useless in dyeing, which combines with bases; the formula of its compound with oxide of lead being  $3PbO, C_{16}H_{10}O_{10}$ .

If safflower, exhausted by cold water, be treated with a solution of carbonate of soda, a red solution is obtained, by accurately neutralizing which with acetic acid, and dipping cotton into it, the red colouring matter, or *carthamin*, is precipitated. As soon as the liquid is nearly bleached, the cotton is removed, and treated with water containing  $\frac{1}{20}$  of carbonate of soda, when the carthamin dissolves, and, if citric acid be added to the liquid, is again precipitated in the form of crimson flakes. The precipitate being redissolved in alcohol and evaporated, a deep-green substance is obtained, which changes colour when seen in different lights. The formula  $C_{14}H_8O_7$  has been assigned to *carthamin*.

#### BRAZIL OR PERNAMBUCO WOOD.

§ 1627. Decoctions of Brazil or Pernambuco wood are used in dyeing, and produce red colours which are not very permanent. The colouring principle of this wood, called *brazilin*, has been obtained in small orange-coloured crystalline aciculæ, soluble in water, alcohol, and ether, but of unknown composition. Brazilin assumes a purple hue on contact with the alkalies, while the action of acid and of ammonia converts it into a new substance, *brazilein*, which is of a deep purple.

#### WELD.

§ 1628. Weld (*reseda luteola*) contains a colouring principle of a beautiful yellow colour, called *luteolin*, which is extracted by boiling water, and appears as a yellow substance, soluble without decomposition, and subliming in small aciculæ. It is very slightly soluble in water, and yet the small quantity which dissolves in it is sufficient to afford beautiful dyes, remarkable for their stability.

#### QUERCITRON.

§ 1629. The name of *quercitrin* has been given to a colouring principle found in the bark of a certain species of oak, the *quercus*



*nigra*, from which it is extracted by treating the powdered bark with alcohol, precipitating the tannin by gelatin, evaporating the liquid, and dissolving the residue in alcohol and then in water. Quercitrin is a yellow crystalline substance, of the formula  $C_{16}H_9O_{10}$ , which dissolves in 100 parts of cold water, and in 4 or 5 of absolute alcohol.

#### ARNOTTO.

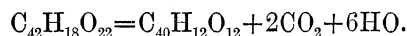
§ 1630. This is the name of a reddish-yellow substance, arising from the fermentation of the *bixia orellana*, and imported from Brazil, Guiana, and the East Indies. Arnotto contains two distinct colouring matters, one of which is yellow, and soluble in water and alcohol, but very slightly soluble in ether; while the other, which is red, is slightly soluble in water, but highly so in alcohol and ether.

#### RED SANDERS.

§ 1631. The name of *santalin* has been given to the collection of colouring matters of the wood of the *pterocarpus santalinus*, and it is extracted by treating this wood, ground to powder, by alcohol, when the solution is of a reddish-yellow colour, and leaves, after evaporation, a resinous substance of the same colour. It dissolves in the alkaline lixivæ, and turns them of a violet colour.

#### INDIAN-YELLOW.

§ 1632. A substance used in dyeing, and known by the names of *purree* and *Indian yellow*, is imported from China and the Indies, but its origin is unknown. It dissolves in water acidulated with chlorohydric acid, while a crystalline substance separates, called *euxanthic acid*, which forms nearly one-half of the weight of Indian yellow; some foreign substances being precipitated at the same time. In order to prepare pure euxanthic acid, Indian yellow is treated with acetic acid, and acetate of lead is added to the liquid, when euxanthate of lead is precipitated, and may be decomposed by sulphuric acid. By boiling the liquid, the euxanthic acid is dissolved, and crystallizes, on cooling, in long, yellow, silky needles, which are readily soluble in alcohol and in ether. Its formula, when dried at  $212^{\circ}$ , is  $C_{42}H_{18}O_{22}$ ; while, if it be heated still further, the euxanthic acid melts and evolves vapours which solidify in small crystals, constituting a new substance, *euxanthone*  $C_{42}H_{12}O_{12}$ , which is also obtained either by the distillation of euxanthate of lead or by causing concentrated sulphuric or chlorohydric acid to act on euxanthic acid. We have, moreover,



Euxanthone possesses no acid properties. With chlorine, bromine, or nitric acid, euxanthic acid yields products by substitution, with the formulæ  $C_{42}H_{16}Cl_2O_{22}$ ,  $C_{42}H_{16}Br_2O_{22}$ ,  $C_{42}H_{17}(NO_4)O_{22}$ . The chlo-

minated and brominated euxanthic acids dissolved in concentrated sulphuric acid, and precipitated by water, yield chlorinated euxanthone  $C_{40}H_{10}Cl_2O_{12}$  or brominated  $C_{40}H_{10}Br_2O_{12}$ .

## CAROTIN.

§ 1633. Carotin, the red-colouring matter of carrots, is extracted by diluting carrot-juice with 4 or 5 times its volume of water, and then adding sulphuric acid, which precipitates the colouring matter with the albumen and fatty substances. The latter are separated by boiling the precipitate for some time with a solution of caustic potassa, which dissolves them; and the carotin is purified by boiling it with dilute sulphuric acid, and digesting it, first with ordinary, and then with absolute alcohol. The substance, when dried, is treated with sulphide of carbon, which dissolves the carotin, after which  $\frac{2}{3}$  of the liquid are separated by distillation, anhydrous alcohol is added to the residue, and the liquid is exposed to the air, when, after some time, small copper-coloured crystals of pure carotin are deposited. Carotin melts at about  $338^\circ$ , but is decomposed at a higher temperature, and it is nearly insoluble in water, alcohol, and ether. Its elementary composition is the same as that of oil of terpentine, but no means of ascertaining its equivalent are known.

## GREEN AND YELLOW COLOURING MATTER OF LEAVES.

§ 1634. The green-colouring matter of leaves, or *chlorophyll*, exists in them but in a very small quantity, and is exceedingly difficult to extract in a state of purity. The best method known consists in digesting the leaves for several days with ether; after which the liquid is filtered and evaporated to dryness, when the greater portion of the residue is composed of a substance analogous to wax and of chlorophyll. It is dissolved in boiling alcohol, which deposits, on cooling, the greater part of the wax; and the alcohol being again evaporated, and the residue treated with a smaller proportion of boiling alcohol, wax still separates on cooling. The solution is finally evaporated, and the residue treated with concentrated chlorohydric acid, which yields a beautiful green solution. The liquid is saturated and filtered, after having introduced some pieces of marble into it, when the chlorophyll, which is rendered insoluble, being precipitated, is washed with weak chlorohydric acid, and then with fresh water.

Chlorophyll is insoluble in water, but readily soluble in alcohol and ether, and sulphuric and chlorohydric acids dissolve it without change; a large quantity of water precipitating it again. From an analysis made of it, the composition of chlorophyll, dried at  $266^\circ$ , would correspond to the formula  $C_{18}H_9NO_8$ .

The name of *xanthophyll* has been given to the yellow-colouring matter of autumnal leaves; but nothing is with certainty known as to its nature.

Vol. II.—3 K

## COCHINEAL.

§ 1635. The cochineal (*coccus cacti*) is a small insect found on the nopal, (*opuntia coccinillifera*), and furnishing the most brilliant red colours for dyeing; those found in commerce being composed only of the dried insects. When these are boiled with water, a red liquid is produced, which is clouded by the addition of alum or bitartrate of potassa; a precipitate being formed which remains a long time in suspension, and which consists of the colouring matter and various fatty and albuminous substances, constituting the *carmine* of commerce. If cochineal be boiled with a weak solution of carbonate of soda, and alum be added to the liquid, red precipitates of alumina, combined with the colouring matter, are formed, known by the name of *carmine lake*.

The name of *carmin* has been given to the colouring matter of cochineal, but it is doubtful whether it has been obtained in a state of purity. The powdered cochineal is treated with ether to dissolve the fatty matters, and then with boiling alcohol to dissolve the carmin, which is deposited during the cooling of the liquid. In order to purify it, it is dissolved in alcohol to which an equal volume of ether has been added, when the carmin is slowly deposited in the form of small purplish-red grains. The substance thus obtained melts at  $104^{\circ}$ , and is soluble in water and alcohol, but insoluble in ether. Acids heighten its red colour, while alkalies turn it of a violet hue.

## ARCHIL AND LITMUS.

§ 1636. The name of *archil* is given in commerce to some very complex colouring substances extracted from various species of lichens, among which may be distinguished the *lecanora parella*, the *variolaria dealbata*, the *roccella tinctoria*, etc. In order to obtain the archil, the lichens are mashed, and macerated in wooden troughs with a mixture of urine and ammonia, or urine and lime, when the substance ferments after some time, and is frequently stirred and kept at a temperature of  $77^{\circ}$  or  $86^{\circ}$ . After several months the archil is ready for commerce, and is put into barrels.

The litmus used in the laboratory is prepared from the same lichens, and by a similar fermentation.

The colouring principles of archil and litmus have hitherto not been isolated with certainty, although several red, non-crystalline substances have been separated, to which various names have been given, but which exhibit none of the characters from which they might be supposed to be definite compounds. But by operating directly on the lichens, perfectly well-defined crystallizable substances have been extracted, from which the colouring matters of archil and litmus probably originate during the fermentation of the plant.

By exhausting the *roccella tinctoria* or the *lecanora parella* by ether, and concentrating the etherial solution by distillation, greenish crystals of an acid substance, termed *lecanoric acid*, are separated, which are purified by washing them with a small quantity of ether and crystallizing them several times in alcohol. Pure lecanoric acid is colourless, and requires for solution 250 parts of boiling water, being still less soluble in cold water; while it dissolves in 15 parts of alcohol and in 80 of ether. It reddens litmus and decomposes the carbonates, and the general formula of its salts is  $\text{RO}, \text{C}_{18}\text{H}_8\text{O}_8$ . If lecanoric acid be boiled for a long time with absolute alcohol, *lecanoric ether*  $\text{C}_4\text{H}_5\text{O}, \text{C}_{18}\text{H}_8\text{O}_8$  is formed, which is separated by evaporating to dryness and again treating with boiling water, which, on cooling, deposits it in the form of small crystals, which may be sublimed without alteration. A *methyllecanoric ether*  $\text{C}_2\text{H}_3\text{O}, \text{C}_{18}\text{H}_8\text{O}_8$  is prepared in the same manner.

§ 1637. Lecanoric acid is decomposed by heat into carbonic acid and a new substance, *orcin*, which volatilizes. It undergoes the same decomposition when heated with the alkalies, or treated even with cold sulphuric acid. The best method of preparing orcin consists in boiling lecanoric acid with an excess of water of baryta, precipitating the baryta by carbonic acid, and filtering the boiling liquid, which, after evaporation, furnishes crystals of impure orcin. These being redissolved in water, the liquid is boiled for some time with alumina or recently precipitated sesquioxide of iron; when the filtered liquor deposits, on evaporation, pure orcin, in long, slightly yellowish prismatic crystals, which first part with water by heat, and then sublime without alteration. Orcin dissolves readily in alcohol. The formula of its hydrated crystals is  $\text{C}_{16}\text{H}_8\text{O}_4, 3\text{HO}$ , and it is precipitated by acetate of lead, furnishing a compound of the formula  $5\text{PbO}, \text{C}_{16}\text{H}_8\text{O}_4$ .

Ammonia, oxygen, and water convert orcin into a colouring substance, *orcein*, which appears to be one of the colouring principles of archil. The reaction is arrested when the substance communicates a beautiful violet colour to the water; for if it were prolonged, new substances would be formed, which would turn the water to a brown colour.

According to an analysis, the formula of orcein would be  $\text{C}_{16}\text{H}_9\text{NO}_7$ ; and it produces, with potassa and soda, violet-red solutions, and with ammonia a beautiful violet colour.

§ 1638. By exhausting the *lecanora parella*, divided into small pieces, by boiling water, a yellowish-brown liquid is obtained, which deposits, on cooling, crystalline flocculi of an acid substance, called *erythric acid*, while the mother liquid contains another substance, *picroerythrin*, which is a product of the alteration of erythric acid by boiling water. Erythric acid is purified by dissolving it in alcohol, and constitutes a white crystalline substance, requiring more than 200 times its weight of boiling water for solution, the greater por-

tion of it being deposited on cooling. It is more soluble in alcohol and in ether, and its solutions redden litmus. Its composition corresponds to the formula  $C_{34}H_{19}O_{15}, 4HO$ ; and when heated, it first melts, and is then decomposed, giving rise to orcin, which sublimes. The cold alkalis dissolve it without change, while if it be heated to the boiling point, orcin and carbonic acid are formed. A solution of erythrate of ammonia, exposed to the air, soon produces a liquid of a deep purple colour.

If erythric acid be boiled with absolute alcohol, a compound, *erythric ether* ( $C_4H_5O + 3HO$ ),  $C_{34}H_{15}O_{11}$ , formerly called *pseudoerythrin*, is formed, which is soluble in boiling water, and separates from it, on cooling, in crystalline aciculæ, or in oily drops which soon become solid.

The picroerythrin remaining in the mother liquid which has deposited the erythric acid, and which is formed directly by boiling erythric acid for a long time with water, differs in its composition from the latter acid only by containing 5 additional equivalents of water, its formula being  $C_{34}H_{24}O_{20}$ . The picroerythrin remains, after evaporation, in the form of a white crystalline mass, which is converted into orcin and carbonic acid, either by heat alone or by boiling it with alkalis.

By exposing erythric acid dissolved in hot water to the air for several days, the liquor turns brown, and then contains two new crystallizable substances, called *amarythrin* and *telerythrin*, the first of which is very soluble in water and alcohol, while the second is insoluble in cold alcohol, thus furnishing an easy means of separating it from the first. The composition of these substances is unknown.

#### INDIGO.

§ 1639. Indigo is found in a great number of vegetables, particularly in plants of the genus *indigofera*, in the *polygonum tinctorium*, and in *woad*; being chiefly obtained from the indigoferous plants. After the flowering of the plant, the leaves which contain the greater proportion of indigo are removed, and dried in the sun; and then they are, after being crushed, infused for 2 or 3 hours with 3 times their volume of cold water. The solution, after being strained through a cloth, is stirred in the air for some time; after which 5 litres of limewater for every 10 kilog. of dried leaves are added, when the liquid soon turns blue and deposits indigo. The deposit is separated, washed with a small quantity of boiling water, and, after being drained on a cloth, is subjected to heavy pressure. This substance, after being dried in the air and cut in pieces, constitutes the indigo of commerce, which is, however, very impure, and contains only about 45 per cent. of real indigo or *indigotin*, the balance consisting of resinous substances, fecula, carbonate of lime, and a large number of other saline substances. In order to remove the

greater portion of these foreign substances, the powdered indigo is washed successively with boiling water, alcohol, and weak solutions of chlorohydric acid.

Pure indigotin is obtained by heating indigo in a glass tube in a current of hydrogen, until crystals begin to sublime in the anterior part of the tube, the temperature being kept as low as possible; when the indigotin volatilizes with a violet vapour, as deep coloured as that of iodine, and is deposited in the form of beautiful crystalline needles of a purplish violet colour. The same vapours are evolved when indigo is thrown on a hot body, but the greater portion of the indigotin is then decomposed.

Indigotin is wholly insoluble in water, and nearly so in alcohol and ether; and its composition corresponds to the formula  $C_{16}H_5NO_2$ .

§ 1640. Dilute acids do not act on indigotin, while concentrated and particularly Nordhausen sulphuric acid dissolve it readily, and produce a beautiful blue liquid; the reaction being not owing to solution, but rather to an actual combination of the indigotin with sulphuric acid.

When indigo is digested with about 5 parts of monohydrated sulphuric acid, raising the temperature to about  $122^\circ$ , the indigo dissolves, and forms a liquid of a very intense purple, depositing a blue precipitate when diluted with water, which is collected on a filter, and washed with water acidulated with chlorohydric acid until the washings contain no more sulphuric acid, when it is dried by heating it to  $248^\circ$  in vacuo. This compound, called *indigo-purple*, or *sulphopurpuric acid*, has the formula  $C_{16}H_5NO_2SO_3$ , and dissolves in pure, but is insoluble in acidulated water. It forms, with the alkalis, purple compounds which are precipitated in flocculi.

By treating, on the contrary, 1 part of indigo with 15 or 20 parts of monohydrated sulphuric acid, or 8 or 10 parts of Nordhausen acid, and keeping the mixture for some time at a temperature of  $122^\circ$  or  $140^\circ$ , a beautifully blue liquid is obtained, which contains another compound of indigotin with sulphuric acid, *sulphindigotic acid*. By adding to this liquid 40 or 50 times its volume of water, a small quantity of indigo-purple, which is collected on a filter, sometimes separates. The liquid being saturated with carbonate of potassa, a precipitate of sulphindigotate of potassa is formed, which is soluble in fresh water, but insoluble in water highly charged with sulphate of potassa. It is washed with a solution of acetate of potassa, which not only dissolves the sulphindigotate, but also removes the sulphate of potassa; and lastly, it is treated several times with alcohol, which removes the acetate of potassa without dissolving the sulphindigotate.

The formula of sulphindigotate of potassa is  $KO.(C_{16}H_4NO_2, S_2O_6)$ , showing the indigo to have lost 1 equiv. of hydrogen, which combined with 1 equiv. of oxygen given off by the sulphuric acid, and which separates in the state of water when sulphindigotic acid

is combined with bases. Several other sulphindigotates may be obtained from the potassa salt by double decomposition.

Lastly, by causing a larger quantity of fuming sulphuric acid to act on indigo, a new acid is formed, together with the sulphindigotic acid, forming, with the alkalies, more soluble salts than the sulphindigotates. This acid, the composition of which is unknown, has received the name of *hyposulphindigotic acid*.

#### *White Indigo.*

§ 1641. When blue indigo is subjected to reducing agents, it combines with the hydrogen set free, and is converted into a colourless substance, called *white indigo*, or *colourless indigotin*, which by exposure to the air again passes into the state of blue indigo. It is prepared by placing in a barrel holding 1 hectolitre, a  $\frac{1}{2}$  kilog. of indigo of commerce, 1 kilog. of sulphate of the protoxide of iron, and  $1\frac{1}{2}$  kilog. of lime; after which the barrel is filled with tepid water, shaken actively, and hermetically closed. After two days, the clear supernatant liquid is drawn off by a siphon, and conveyed into large bottles filled with carbonic acid, at the bottom of which acetic or chlorohydric acid, charged with sulphuric acid in sufficient quantity to saturate the lime, has been placed. The liquid immediately becomes clouded, grayish-white flakes being precipitated, which are collected on a filter and rapidly washed, first with water charged with sulphurous acid, and then with recently boiled fresh water. The filter is expressed between tissue-paper and the substance dried in vacuo.

This substance is white indigo, but it is very difficult to prevent it from absorbing a small quantity of oxygen from the air, and it should be kept in bottles filled with carbonic acid. It is insoluble in water, soluble in alcohol and ether, does not act on litmus, and is decomposed by heat. It rapidly turns blue in water containing air, and does not combine directly with the weak acids; although during the reduction of sulphindigotic acid by sulphydric acid a colourless substance is obtained, which is probably a compound of colourless indigo with sulphuric acid. Nordhausen acid dissolves it, but the liquid is of a beautiful purple colour; and all oxidizing agents convert it instantly into indigo-blue. White indigo readily combines with bases, furnishing several soluble compounds; which is the case with the alkalies, ammonia, lime, baryta, and magnesia; the solutions being yellowish, but soon turning blue in the air. The other metallic oxides form insoluble compounds, which are easily obtained by double decomposition. The composition of white indigo corresponds to the formula  $C_{16}H_6NO_2$ , and differs from that of blue indigo  $C_{16}H_4NO_2$  only by containing 2 additional equivalents of hydrogen.

*Products of the Action of Nitric Acid on Indigo.*

§ 1642. The action of nitric acid on indigo produces *isatin*  $C_{16}H_5NO_4$ , remarkable for the numerous substances which have been derived from it. A liquid paste is made with 1 kilog. of indigo of commerce and water, which is carefully heated in a porcelain capsule, nitric acid being gradually introduced with constant stirring, until 600 or 700 gm. of acid are added. The indigo has then disappeared, and the liquid, which is more or less brown-coloured, contains the isatin, mixed with several other substances, which have not yet been examined. The liquid, being diluted with a large quantity of water, is heated to boiling, and the boiling liquid rapidly filtered, when the isatin is deposited, on cooling, in reddish mamillary crystals. The deposit remaining is heated with the mother liquid which has deposited the first crystallization of isatin, which furnishes an additional quantity; and this process is repeated until no more isatin is deposited.

Isatin may also be obtained by heating indigo with a mixture of bichromate of potassa and sulphuric acid, dissolved in 20 or 30 parts of water.

Isatin is slightly soluble in cold water, but largely so in boiling water, and still more freely in boiling alcohol; and its solutions do not act upon litmus. When heated, it first melts, and then gives off vapours of unaltered isatin, the greater portion of the substance being nevertheless decomposed, and leaving a copious carbonaceous residue. Concentrated nitric acid, when cold, readily dissolves isatin, forming a brownish-red liquid, which deposits unaltered isatin; while if the liquid be boiled, lively reaction ensues, and oxalic acid is formed.

Isatin is easily acted on by chlorine, and yields products derived by substitution. The isatin must be diluted with water, and a current of chlorine passed through, when *monochlorinated isatin*  $C_{16}H_4ClNO_4$  is first formed; while if the action of the chlorine be prolonged, *bichlorinated isatin*  $C_{16}H_3Cl_2NO_4$  is produced; the same compounds being obtained by causing chlorine to act on indigo. Bichlorinated isatin is more soluble in water and in alcohol than monochlorinated isatin. Isatin and indigo, in contact with melted hydrate of potassa, evolve hydrogen, and anilin is formed, (§ 1684;) while, under similar circumstances, monochlorinated isatin produces monochlorinated anilin, and bichlorinated isatin bichlorinated anilin.

When a concentrated solution of potassa is poured over isatin, there results first a violet-coloured liquid, which by boiling, and after being diluted with water, is converted into a yellowish solution, depositing crystals on evaporation. Here isatin has seized upon the elements of 1 equiv. of water, and been converted into a new acid, called *isatic*, the formula of isatate of potassa being  $KO, C_{16}H_6NO_5$ .



With ammonia, isatin and isatic acid form numerous compounds, which will not occupy our attention.

By subjecting isatin to the action of reducing agents, it is changed into *isathyd*  $C_{16}H_6NO_4$ , by a reaction precisely similar to that which converts blue into white indigo. Sulfhydrate of ammonia being poured into a hot alcoholic solution of isatin, and the mixture allowed to rest for some days in a well-corked bottle, sulphur is deposited, at the same time with laminated crystals of isathyd, which are colourless or slightly grayish. They are insoluble in water, but slightly soluble in boiling alcohol, from which they are deposited on cooling; and they are decomposed by heat. By treating monochlorinated and bichlorinated isatin in the same manner, there results *monochlorinated isathyd*  $C_{16}H_5ClNO_4$  and *bichlorinated isathyd*  $C_{16}H_4Cl_2NO_4$ .

If sulfhydric acid be substituted for sulfhydrate of ammonia, the isatin is not satisfied with 1 equiv. of hydrogen, but also exchanges 2 equiv. of oxygen for 2 equiv. of sulphur, and furnishes a new substance, *bisulphisathyd*  $C_{16}H_6NO_2S_2$ , which, when treated with an alcoholic solution of potassa, forms a red liquid, depositing colourless crystals of *sulphisathyd*  $C_{16}H_6NO_3S$ .

If, on the contrary, the bisulphisathyd be heated with a highly concentrated solution of potassa, the 2 equiv. of sulphur are removed, and a rose-coloured liquid is obtained, holding a rose-coloured substance in solution, of the same elementary composition with white indigo, and which has received the name of *indin*.

#### ACTION OF VEGETABLES ON THE ATMOSPHERE.

§1643. Vegetables derive the materials necessary for their growth, principally from the atmosphere; but as the various circumstances of this phenomenon are not well understood, we shall only mention what is most accurately known on the subject.

All vegetables spring from a seed which is the product of a similar vegetable, and if properly dried and preserved from moisture and the attacks of insects, appears to be able to retain its germinating principle for an indefinite length of time. But if it come into contact with water, and the temperature be not too low, it soon swells, while its woody envelope cracks, and filaments, or *radicles*, which endeavour to penetrate the earth, start from one side, and from the other rises a small stem, the *germ*, in an opposite direction, into the air. These primary developments of vegetable life take place at the expense of the amylaceous matter of the seed, in which is formed a nitrogenous principle, called *diastase* in the cerealia, the special office of which is to convert rapidly the starch into dextrin and sugar, that is, into soluble principles, which, by means of agencies as yet unknown, are again organized, and transformed into cellulose, in its turn serving for the formation of the primary

cellular tissues of the germ and radicles. During this first epoch of vegetable life, carbonic acid is disengaged, and the presence of oxygen appears essential, for moistened seeds will not germinate in an atmosphere deprived of this gas. The portions of the seed which furnish the amylaceous substance, the *cotyledons*, have then lost their consistence, and wither.

When it reaches the air, the germ assumes a green colour, and throws out the primary leaves. The phenomena of assimilation are then wholly changed, and the new vegetable seeks the elements necessary to its growth, principally in the atmosphere; and its green portions, the leaves chiefly, under the influence of solar light, absorbing the carbonic acid of the air, assimilate to themselves the carbon, and give out oxygen into the atmosphere; while they also possess themselves of a certain quantity of nitrogen, which serves for the formation of the nitrogenous principles essential to them. The hydrogen is evidently furnished by the water which arises both from the vapour disseminated in the atmosphere and the moisture of the soil. The greater portion of the water remains as such in the vegetable, and forms the sap, which serves to transport, through the various parts of the plant, the nutrient principles, rendered soluble by actions at present unknown; while another part of the water is probably decomposed, by the action of the vegetative forces, into hydrogen which is assimilated, and into oxygen which is disengaged with that arising from the more or less complete decomposition of the carbonic acid.

§ 1644. In this theory of vegetable growth, we have supposed the earth to play but an unimportant part, and to serve merely as a base on which the plant is erected, and whence, by means of its roots, it can procure the greater portion of water necessary for sap; but the daily experience of the farmer proves that its part is less passive. When the soil is deprived of organic substances in decomposition, it is known to have lost its fertility, and to give birth to a small number of dwarfish plants, which struggle with difficulty through the various phases of an ephemeral existence; and in order to restore its fertility, it must be supplied with organic detritus, principally animal substances, known by the name of manures. Manures supply the roots with organic, chiefly nitrogenous substances, which the vegetable assimilates to itself; while they also furnish mineral principles, either already soluble or rendered so by the chemical agencies developed in the earth. These constituents, which are found again in the ashes of the vegetable, are necessary to its well-being; and when they are wanting in the soil, or do not exist in sufficient quantity, the plants wither, and are unable to construct the mineral framework which appears to be essential to some of them.

§ 1645. The following are some experiments in support of this theory:—

The decomposition of carbonic acid by the green portions of vegetables can be very easily demonstrated. By placing fresh leaves in a bell-glass, partly filled with water, and partly with carbonic acid gas, and exposing the glass to the sun, the carbonic acid disappears, and after some time is replaced by a rather smaller quantity of oxygen; and as carbonic acid contains a volume of oxygen equal to its own, we may conclude from this experiment that all the oxygen of the carbonic acid is not set free. The carbonic acid, very probably, is only partially decomposed by the vegetable, being, for example, reduced to the state of carbonic oxide, which enters into the constitution of new organic substances, the remainder of the oxygen arising from the decomposition of the water. If part of a branch of a tree be placed in a bell-glass exposed to the sun, and into which has been introduced a mixture in known proportions of atmospheric air and carbonic acid, it will be easy to ascertain that the gas which escapes from the bell-glass is almost wholly deprived of its carbonic acid, and that the latter is replaced by oxygen.

This decomposition of carbonic acid by the leaves takes place only under the influence of the solar rays and the diffuse light of day; while in the dark, or when exposed to artificial light, an inverse action ensues. Experiment shows that in this case, they evolve carbonic acid and absorb oxygen, while if the effects of the day be compared with those of the night, the former will be found to exceed the latter greatly, and consequently the action resulting is that which takes place under the influence of the solar rays. Those parts of the vegetable which are unprovided with the *green parenchyma*, the roots, chiefly behave with regard to the atmospheric air, even in the sun, like the green parts in the dark, since they absorb oxygen and evolve carbonic acid. The absorption of oxygen appears to be essential to them, for a vegetable soon perishes when its roots are in an atmosphere deprived of this gas.

The following experiment proves very conclusively the manner in which a plant grows at the expense of the elements of atmospheric air:—A known weight of seed is sown in a soil formed of pounded bricks or quartzose sand previously calcined and washed, this artificial soil being placed under a bell-glass so arranged as to be kept properly moist, and exposed to the sun, while a current of air, to which 1 or 2 hundredths of carbonic acid gas are added to assist the development of the vegetable, is passed through the bell-glass. The seeds soon germinate, the plants grow, and pass through the various phases of vegetable life, without, however, ever attaining the development and strength they would have acquired in a fertile soil. They are then removed, and the absolute quantities of carbon, hydrogen, oxygen, and nitrogen which they contain are ascertained by chemical experiment. It is evident that the soil could afford them nothing, as it is unchangeable, and at all events contains neither

carbon nor nitrogen; and therefore, if they have not borrowed their carbon and nitrogen from the air, they can contain only the carbon and nitrogen which existed in the seeds. Now, it is easy to analyze a sample of seed identical with that which has germinated, and determine by calculation the carbon and nitrogen contained in the seeds which have vegetated; and by comparing this quantity of carbon and nitrogen with that found in the plants, the latter will be found to be much larger. It must therefore be admitted that the plant has absorbed carbon and nitrogen from the atmosphere.

§ 1646. We have shown (§ 95) that atmospheric air contains only from 4 to 6 ten-thousandths of carbonic acid, which very small proportion is still sufficient to furnish the carbon which accumulates in the vegetables covering the earth. But the carbonic acid of the air, which thus disappears, is constantly reproduced and restored to the atmosphere by the respiration of animals, the decomposition of vegetables, and the chemical reactions taking place in the interior of the globe. Moreover, the terrestrial atmosphere is of considerable extent, and the total amount of carbonic acid which it contains includes a quantity of carbon greater than the whole vegetable kingdom; and the continual agitation of the atmosphere mixes all its component parts, and assists the absorption of carbonic acid by plants by constantly renewing the air which surrounds them.

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#### ANIMAL CHEMISTRY.

§ 1647. The body of every animated being may be considered as a laboratory in which extremely numerous chemical reactions are performed, the majority of which are very complicated and as yet but little understood; as well upon the substances which already constitute the being, as on the new substances taken in as food. In the present state of science, it is impossible to decide whether all these reactions are owing, solely, to forces of the same nature as those which determine the chemical metamorphoses witnessed in the laboratory, or the unknown and undefinable cause, which is called *life* or *vitality*, introduces into it some special forces.\* Even admitting that we can explain, without resorting to other agents than the ordinary chemical forces, all the chemical modifications of substances in the vegetable or animal economy, we should still be obliged to admit the existence of special, and so to say, *intelligent* actions, in order to explain the varied, and yet so clearly marked forms which solid matter assumes in the composition of the various

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\* We use here the word *forces*, because it is generally used in this sense; but it must not be forgotten that it in no wise satisfies the definition of it given in mechanics. It merely expresses the efficient and unknown cause of complicated effects, the exact analysis of which is at the present day as yet impossible.

organic forms, so different from those assumed by matter when it simply obeys the laws of molecular attraction, without regard to the organism. A single substance, modified by the vital forces, may assume the most varied organic forms, and different states of aggregation, which frequently alter its apparent properties so greatly as to lead us, at first sight, to consider them as different substances. The progress of substances in the economy is governed by laws and directed by mechanical arrangements, generally of difficult explanation, and acting by instinct, which impel these substances successively into the vessels in which they are elaborated and fitted for the special functions assigned to them in the organism.

The study of the modification of matter in the vegetable and animal economy, therefore, presents difficulties much greater than those of the chemical phenomena observed in the laboratory. They occur between substances generally of very complex composition, of extreme mobility, and difficult definition by the characters we have adopted for mineral substances. At each step we meet with those mysterious agencies, by which very small quantities of certain substances of a nature still problematical, execute, without any apparent intervention of their chemical elements, reactions between incomparably larger quantities of other substances: phenomena of which many examples have already been mentioned in the present work, and from the explanation of which chemists generally extricate themselves by calling them *phenomena of contact*, or *fermentations*.

Again, other circumstances increase the difficulty of this study. Substances are modified in the animal and vegetable economy, successively, and in special organs which it is impossible to detach from the organized being in order to study the reactions which take place in each of them, without altering completely the conditions which would have existed in the animated being. Lastly, in the laboratory, chemical reactions are studied in unassailable vessels which play no part in the phenomena, which is altogether different in organized beings, chemical reactions being there effected in vessels the substance of which, for the most part, shares in the reaction, and thus immeasurably complicates the phenomena.

We have been satisfied with describing the substances of vegetables, uninfluenced by vegetative life, and have not touched upon their modifications in the plant, since we could have advanced but a few vague and uncertain notions. Our knowledge of the modifications of substances in the animal economy are not much more accurate; and to avoid the danger of stating any rash opinions, we should observe the same caution, and only describe the property of those substances when they are no longer influenced by vitality. But here the question becomes much more important, on account of its intimate connection with the medical sciences, in which our acquaint-

ance with the chemical reactions ensuing in the human body in health or in disease is of the highest importance, inasmuch as it may furnish valuable means of diagnosis, or may discover the treatment applicable to various pathological conditions.

We shall describe the most important and best-known animal substances, with their properties, when they are uninfluenced by vitality; and then endeavour to give a general idea of the opinions on the chemical phenomena which take place in the economy.

#### SOLID ANIMAL SUBSTANCES.

§ 1648. We shall begin with the study of the solids which form the various organs of animals, and constitute, as it were, the laboratory and apparatus in which are performed the great phenomena of life. We shall divide them into the bones, teeth, cartilages, the corneous tissue, the skin, and the various membranes, muscular flesh, fatty substances, and the cerebral substance.

§ 1649. BONES.—Bones form the framework, or what is called the *skeleton* of vertebrated animals. They are composed of an organic portion, the *cartilaginous substance*, and of earthy matter, consisting chiefly of carbonate and phosphate of lime, and constituting in the mammiferæ about  $\frac{2}{3}$  of the weight of the bone. The bones are covered externally with a fibrous membrane, the *periosteum*, which contains the external blood-vessels distributed to the bones, and supplies them with matter for increment. Internally is found another membrane, the *medullary*, which also receives blood-vessels.

When a bone is suspended for several days in a weak solution of chlorohydric acid, the earthy salts are dissolved, and there remains only the cartilage, retaining exactly the shape of the bone, but reduced to a soft and translucent substance. It is necessary to renew the liquid several times, and lastly to wash the cartilage with fresh water until no traces of acid remain. When dried, the cartilaginous substance partly loses its translucency and becomes brittle. Ether separates a small quantity of fatty matter from it.

Cartilage is insoluble in cold water, but ultimately dissolves wholly in boiling water, being converted into a substance commonly called *gelatin*. We subjoin the average composition of the bones of an adult man and that of an ox, in a state of health:

	Man.	Ox.
Organic matter.....	33.30	33.30
Basic phosphate of lime with a small quantity of fluoride of calcium.....	53.04	57.35
Carbonate of lime.....	11.30	3.85
Phosphate of magnesia.....	1.16	2.05
Soda and chloride of sodium.....	1.20	3.45
	<hr/> 100.00	<hr/> 100.00

The composition of the bones of the other mammalia and of birds is analogous, while in fishes the proportion of the organic and earthy

matters varies considerably, and they may be divided into *bony fishes*, whose bones contain large quantities of calcareous salts, and *cartilaginous fishes*, whose bones are nearly destitute of these salts. The proportion of cartilaginous matter being always greater in the bones of fishes than in those of other vertebrated animals, the former are the more flexible.

§ 1650. TEETH.—The composition of the teeth of the mammalia does not differ much from that of their bones, as will be seen from the following analysis:

	Man.	Ox.
Cartilaginous matter .....	28.0	31.0
Phosphate of lime, with fluoride of calcium.....	64.3	63.1
Carbonate of lime .....	5.3	1.4
Phosphate of magnesia .....	1.0	2.1
Soda with a small quantity of chloride of sodium...	1.4	2.4
	<u>100.0</u>	<u>100.0</u>

The part of the tooth beyond the gum is covered with a white, very hard enamel, almost wholly composed of phosphate of lime, carbonate of lime, and a small quantity of fluoride of calcium. The enamel of human teeth has been found to contain about 90.0 of calcareous and magnesian phosphates, and 8.0 of carbonate of lime.

§ 1651. CARTILAGES.—The name *cartilage* has been given to a dry, elastic tissue, containing only a few hundredths of earthy salts, and very widely distributed in the animal economy, sometimes serving to connect the ends of bones which move on each other, and sometimes being prolongations of the bones, as in the ribs, for example, and furnishing them an elasticity suitable to their functions; while it finally sometimes forms the solid part of certain organs, as the nose, ear, the trachea, etc. The chemical nature of all cartilages does not appear to be the same, for while some seem to be identical with the cartilage of the bones, and are converted, by boiling water, into gelatin, others, such as the cartilages of the nose and ear, do not undergo this transformation. Cartilages are characterized by corpuscles of peculiar form, called *cartilaginous corpuscles*.

§ 1652. CORNEOUS, OR HORNY MATTER.—The horns, nails, claws, and hoofs of animals are formed of substances possessing very similar properties, and which hitherto have been regarded as identical: they are designated by the general name of *horny matter*. They are insoluble in water, and soften in boiling water, and their composition is as follows:

	Cow Horns.	Buffalo Horns.	Human Nails.
Carbon .....	50.8	51.4	51.1
Hydrogen.....	6.8	6.8	6.8
Oxygen.....	23.5	24.4	25.2
Sulphur .....	2.6		
Nitrogen.....	16.3	17.4	16.9
	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>

§ 1653. HAIR, FEATHERS, SCALES.—Human hair, as well as that of animals, is composed of an organic matter which does not appear to differ essentially from horn in its chemical composition and its behaviour with reagents. They contain several fatty substances, generally coloured, from which their hue is ordinarily derived. The feathers of birds closely resemble horn; the same being true of the scales of reptiles. For want of accurate experiments, the identity of all these substances is admitted.

The composition of fish-scales, on the contrary, resembles that of bone, since they contain 40 to 50 per cent. of phosphate of lime, from 3 to 10 per cent. of carbonate of lime, and from 40 to 55 per cent. of organic matter.

§ 1654. SKIN AND MEMBRANES.—The skin of animals is divided into three principal parts: 1st, the skin, properly so called, or *derma*, which envelops immediately the muscles and bones; 2dly, the *papillary tissue*, formed by a delicate, extremely sensible tissue, traversed by small blood-vessels and nerves, and containing the pigment which colours the skin so variously in the different races of men throughout the globe; and, 3dly, the outer covering, or *epidermis*, a simple pellicle, very thin, but very resisting, pierced by numerous small orifices, through some of which the hairs pass, while others give exit to the fluids of perspiration; and still others allow certain fatty substances to exude. The skin, which is soft and flexible when washed in water, becomes hard and coriaceous by drying. When dipped in a solution of tannin, it combines with it without falling to pieces, and becomes imputrescible, which constitutes the process of *tanning*. When boiled with water it dissolves entirely into a gelatinous substance, commonly called *glue*; but the transformation does not take place in the mucous membranes, which appear to consist of substances differing from those of the skin.

§ 1655. MUSCULAR TISSUE.—Meat, or flesh, is the collection of several organs, called *muscles*, each of which is formed by an assemblage of fibres united in bundles. A multitude of nerves and canals, through which various fluids circulate, traverse this tissue in all directions; thus rendering muscular flesh a very complicated assemblage. The substance which constitutes the muscular network is called *fibrin*, which of itself is colourless; flesh owing its red colour to the blood which fills an infinity of small capillary vessels distributed throughout it.

One hundred parts of beef are reduced, by desiccation, to 25 parts, and, after incineration, there remains about  $1\frac{1}{2}$  part of salts, composed chiefly of phosphates of potassa, soda, and lime, and a small quantity of alkaline chlorides.

By exhausting finely chopped beef by cold water, about 6 hundredths of it are dissolved, one-half of which is composed of albumen, and other materials of the blood coagulable by heat. If therefore the liquid be boiled, there remains in solution only 3 hun-



dredths of matter, composed of soluble alkaline salts, a crystallizable nitrogenous substance, called *creatin*, (from *κρεας*, flesh,) and salts formed by a peculiar organic acid, called *inosic*. If, on the contrary, flesh be treated with hot water, the albuminous substances coagulate immediately, and the same substances dissolve as in cold water; while, if the ebullition be prolonged, a small quantity of gelatin is dissolved in addition, as is the case in making soup. A portion of the fat is also forced from its cells, and floats on the surface of the liquid.

Muscular flesh yields *leucin* (§1278) by being boiled with dilute sulphuric acid.

§ 1656. *Fibrin*.—It is difficult to separate fibrin from muscular flesh, because it is intimately mixed with other substances which behave in a very analogous manner toward chemical agents.

It is generally extracted from freshly drawn blood by beating it with rods, to which the fibrin adheres in the form of long colourless filaments. They are washed with much water, to detach the other soluble or insoluble principles of the blood; and then, after being dried, they are treated with alcohol and ether, which remove the fatty matters. The fibrin is then washed with a very dilute solution of chlorohydric acid, and, lastly, with distilled water.

Fibrin is a white, tasteless, and inodorous substance, completely insoluble in water, alcohol, and ether, and, by drying, assuming a horny consistence. Prepared in the method just stated, it leaves 2 or 3 per cent. of ashes, composed chiefly of calcareous and magnesian phosphates. A long boiling with water alters it and dissolves a portion of it; and when left in water and exposed to the air it soon putrefies, but may be preserved for an indefinite length of time in alcohol. Acids convert it into a gelatinous mass, insoluble in acid liquids, but soluble in fresh water, while it dissolves readily in alkaline lyes, even when they are diluted; and if the solution be saturated with an acid, a precipitate is formed, which, however, cannot be considered as the original fibrin.

According to the most reliable analyses of fibrin, it contains

Carbon .....	62.78
Hydrogen.....	6.96
Nitrogen.....	16.78
Oxygen .....	13.48
	<hr/>
	100.00

§ 1657. *Albuminous Substances*.—We shall not here again refer to the albuminous substances, which have been sufficiently described, (§1279.) Their identity in the two kingdoms, though far from being demonstrated, is generally admitted.

§ 1658. *Creatin*  $C_8H_9N_3O_4$ .—In order to obtain creatin, finely chopped meat is treated with an equal weight of cold water; and after having stirred the mixture for some time, it is expressed in a

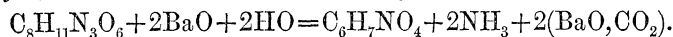
canvas bag, the filtered liquid being used in treating an additional quantity of meat. The liquid, being then heated to  $212^{\circ}$  in a water-bath, in order to coagulate the albuminous substances, is evaporated after being filtered, and the new deposits which form are separated. When the liquid is reduced by evaporation to  $\frac{1}{2}$  of its volume, water of baryta is added, furnishing a precipitate of various phosphates and sulphates, which are to be separated. The evaporation is continued until the liquid is reduced to  $\frac{1}{10}$  of its original volume, and it is then allowed to evaporate spontaneously in a warm place, when crystalline aciculæ of creatin are formed, which are to be washed in cold water and alcohol, and redissolved in boiling water, which, on cooling, deposits them in a state of purity.

Lean meat is best adapted to this purpose, that of fowls and the weasel yielding the largest proportion of creatin: 100 kilog. of beef yield 62 gm., and 100 kilog. of horseflesh have furnished 72 gm.

Creatin is a neutral, inodorous, and colourless substance, soluble in 75 parts of cold and in a much smaller quantity of boiling water; and separating, on cooling, from its saturated aqueous solution, in the form of prismatic crystals, which lose 18 per cent. of water when dried at  $212^{\circ}$ . It dissolves in 90 parts of absolute alcohol; and the formula of crystallized creatin is  $C_8H_9N_3O_4 + 2HO$ .

Creatin is not affected by very dilute acids, while concentrated acids abstract 4 equiv. of water from it, and convert it into a substance  $C_8H_7N_3O_2$ , or *creatinin*, which is a true organic alkali, possessing a very strong alkaline reaction comparable with that of ammonia, and forming crystallizable salts with all the bases.

Creatin also dissolves without alteration in very dilute alkaline lyes, while the concentrated alkalies decompose it, ammonia being evolved, besides carbonic acid which combines with the alkali, and a new organic base, *sarcosin*  $C_6H_7NO_4$ . The decomposition is generally effected by boiling creatin with a concentrated solution of baryta, the reaction being expressed by the following equation:



Sarcosin crystallizes in right prisms, with a rhombic base; exerts no reaction upon coloured reagents; but forms crystallizable salts with several of the acids. It is insoluble in alcohol and ether.

§ 1659. *Inosic Acid*  $C_{10}H_6N_2O_{10}, HO$ .—This acid remains in the mother liquid which has deposited creatin, and is extremely soluble in water; while, if alcohol be added, the liquid becomes milky, and in the course of a few days small yellowish crystals of inosate of potassa, or baryta, if the latter base has been used in the preparation of the creatin, are developed. The crystals being redissolved in boiling water, and chloride of barium added, crystals of inosate of baryta are deposited, on cooling, which may be purified by several crystallizations, and then take the formula  $BaO, C_{10}H_6N_2O_{10} + 7HO$ .

By decomposing it by sulphuric acid, free inosic acid is obtained, which does not crystallize in an aqueous solution unless alcohol be added. The formula of inosate of silver is  $\text{AgO}, \text{C}_{10}\text{H}_6\text{N}_2\text{O}_{10}$ .

§ 1660. *Gelatinous Substances*.—We have mentioned that the skin, the cartilaginous substance of the bones, and the cartilages properly so called, when boiled with water, ultimately dissolve wholly, and form a viscous liquid, which becomes gelatinous on cooling. For a long time it was supposed that all the substances formed under these circumstances were identical, and the general name of *gelatin* was assigned to them; but it is now admitted that there are two: one being afforded by the skin, intestinal membranes, and tendons, which has retained the name of *gelatin*, while the other, called *chondrin*, is furnished by the cartilaginous substance.

The chemical reactions and composition of these two substances differ from each other, since solutions of chondrin are precipitated by sulphate of alumina, alum, and sulphate of iron, which do not affect solutions of gelatin. The formula  $\text{C}_{35}\text{H}_{26}\text{N}_4\text{O}_{14}$  has been given to chondrin, and that of  $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_5$  to gelatin; but these formulæ are very uncertain, because there are no means of ascertaining the purity of the substances and of determining their equivalents, no definite compound with them being known with certainty. In the applications of the two substances no distinction is made, and they are generally indiscriminately called gelatin and glue.

Pure gelatin is colourless and transparent, as is the case in the *fish-glue*, or *ichthyocolla*, found in commerce. When heated it melts, and congeals on cooling into a remarkably coherent mass. Cold water merely softens and swells, without dissolving it, while boiling water dissolves it, and forms a viscid liquid, which coagulates into a more or less consistent jelly on cooling. Alcohol precipitates gelatin from its aqueous solution. Prolonged ebullition with water destroys gelatin, and it afterward no longer coagulates. We have already said (§ 1458) that tannin completely precipitates gelatin from its solutions.

§ 1661. Glue is manufactured from leather scraps, tendons, horns, and hoofs of animals. As animal substances putrefy readily, they are soaked, if they cannot be immediately used, for 15 or 20 days in milk of lime, and then dried in the air, which prevents their fermentation. When required for use they are digested for some time in water, which causes them to swell and removes the lime.

Animal substances intended for the manufacture of glue are placed in boilers with water, rapidly heated to boiling, which is stirred, from time to time, the operation being continued until a portion of the liquid taken from the kettle congeals on cooling. The liquid is then decanted into a second kettle, kept at a temperature of nearly  $212^\circ$ , in order that the liquid may not become too viscid before depositing the substances it holds in suspension; and after some hours, it is run into moulds made of pine-wood, and

allowed to cool. When the glue sets, which generally takes place in 15 or 18 hours, the moulds are carried to a well-ventilated and cool drying-room, where the glue is separated by a flexible and wetted knife, and spread upon a table likewise wetted. It is immediately cut into small sheets by means of a brass wire, and spread on nets to dry, whence commercial glue usually shows the prints of the threads of the net. The residue in the boiler, treated with a fresh quantity of boiling water, may afford more glue.

§ 1662. Gelatin is extracted from bones by two different processes. In the first, the bones are subjected to the action of steam, under high pressure, in a Papin's digester, when the greater part of the gelatin dissolves in the water, while the bones still retain a sufficient quantity to allow of their being used in the manufacture of animal black. If it be desired to prepare gelatin for alimentary purposes, the temperature should not be raised above  $223^{\circ}$  or  $226^{\circ}$ , and beef-bones only should be used, because the bones of sheep or hogs would give the gelatin a disagreeable taste and smell.

By the second process, which yields more gelatin than the preceding, the bones are crushed between rollers and boiled for some time with water, in order to extract the grease which is separated. They are then digested for 24 hours with a dilute solution of chlorohydric acid, which dissolves the calcareous salts; for which purpose a weight of chlorohydric acid, at  $22^{\circ}$  Baumé, equal to that of the bones, is used, but it serves for several times. The bones, deprived of their calcareous salts, are washed until the water is free from acidity; after which they are boiled with water in a cast-iron kettle. Not more than the quantity of water necessary to obtain a solution of gelatin which will set on cooling should be used, and added at 3 different times, because the solution of gelatin is injured by too long boiling.

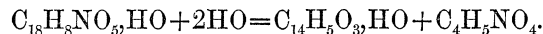
Fish-glue, or *ichthyocolla*, is prepared from the swimming-bladder of the sturgeon by merely drying it; and is chiefly used in refining wines; but pure gelatin, obtained from bones, will answer the same purpose. Fish-glue softens in cold water, and readily dissolves when the temperature is raised. When poured into a slightly acidulated liquid the solution coagulates, and its filaments carry down, as in a net, the mucilaginous substances in the liquid.

Mouth-glue is made of a concentrated solution of gelatin, with the addition of a small quantity of sugar and gum-arabic; the solution being boiled in order to dissolve the gelatin completely, and the liquid poured into moulds made of oiled paper, where it becomes solid.

§ 1663. *Sugar of gelatin, or glycocoll*,  $C_4H_5NO_4$ .—Sulphuric acid effects a very remarkable change in gelatin, and converts it into a crystallizable substance of a sweet taste, acting the part of a feeble alkali, and called *glycocoll*, or, more improperly, *sugar of gelatin*. In order to prepare it, 1 part of gelatin is digested

for 24 hours with 2 parts of concentrated sulphuric acid, and 10 parts of water being added, it is boiled for 5 hours. The liquid, saturated with chalk, and then evaporated to the consistence of syrup, deposits, after some time, crystals of glycocoll; their formation taking place very slowly, sometimes requiring a whole month for completion. Boiling alkaline solutions effect the same change in gelatin, in which case ammonia is disengaged.

But the best method of preparing pure glycocoll consists in boiling, with 4 times its weight of concentrated sulphuric acid, a peculiar acid found in the urine of herbivorous animals, which we shall soon describe under the name of *hippuric*. Hippuric acid  $C_{13}H_8NO_5$ , HO then separates into benzoic acid  $C_{14}H_5O_3$ , HO, which is almost wholly deposited on the cooling of the liquid, and into glycocoll  $C_4H_5NO_4$ , which remains in solution in combination with the chlorohydric acid. The chlorohydrate of glycocoll is evaporated to dryness in a water-bath, and purified by several crystallizations in water, after which it is supersaturated with ammonia, and again treated with highly concentrated alcohol, which precipitates the glycocoll in the form of small crystals. The reaction is expressed by the following equation:



Glycocoll is a white substance, having a sweet taste, but which does not ferment. It is soluble in water, nearly insoluble in alcohol and ether, and forms crystallizable compounds with the majority of the acids, without exerting any action on red litmus. It also combines with potassa and several metallic oxides.

§ 1664. FATTY SUBSTANCES.—We shall not again refer to the fatty substances which are found in animals, since they are identical with those existing in vegetables, and which have been minutely described (§ 1590 *et seq.*)

§ 1665. CEREBRAL SUBSTANCE.—The cerebral substance is composed essentially of,

1st. A solid fat acid, containing phosphorus, and called *cerebric acid*;

2d. A liquid fat acid, also containing phosphorus, called *oleophosphoric acid*;

3d. A peculiar fatty matter, or *cholesterin*, which shall be described when treating of bile;

4th. Small quantities of ordinary fatty substances, such as stearin, margarin, and olein.

Cerebric acid is a white substance, which may be obtained in crystalline granules, dissolving readily in alcohol and boiling ether, while cold ether retains but a small quantity of it. It melts when heated, and is very easily decomposed. It combines with bases without forming crystallizable salts, and its analysis exhibits

Carbon.....	66.7
Hydrogen.....	10.6
Nitrogen.....	2.3
Phosphorus.....	0.9
Oxygen.....	19.5
	<hr/> 100.0

But it is difficult to decide whether the matter subjected to analysis was a simple substance.

Oleophosphoric acid is a yellowish oil, insoluble in water and cold alcohol, but very soluble in boiling alcohol and ether. It combines with bases, but forms no crystallizable salts. By contact with water, it is spontaneously decomposed into phosphoric acid, which dissolves, and an oily substance analogous to and perhaps identical with olein.

#### OF CERTAIN CHEMICAL PHENOMENA WHICH OCCUR IN THE ANIMAL ECONOMY.

§ 1666. The substances we have just enumerated form the laboratory and apparatus in which all the chemical reactions of the economy take place; but it is important to remark that these substances do not act an inert or merely formal part; influenced by the nervous system, they not only assume the shapes and movements necessary for the circulation of the fluids, but also intervene in the chemical reactions by being constantly dissolved and renewed. We shall give the general name of *nutrition* to the collection of chemical phenomena which occur successively in alimentary substances, from the moment they are taken into the mouth, until, after having traversed the whole of the general circulation, they are rejected in the gaseous state, with the air expired, or in the state of solids and liquids, in the urine or excrements.

The phenomena of nutrition, starting from the ingestion of food, follow and succeed each other in this order:

- 1st. Digestion,
- 2d. Respiration,
- 3d. Circulation,
- 4th. Excretion.

§ 1667. We shall give an idea of the various apparatus in which these phenomena are produced, by describing the liquids arising from the decomposition of the alimentary substances, and to which physiologists attribute the chief modifications of these substances in the economy. In order to render our explanation more clear, we have figured (fig. 686) the various organs and circulatory apparatus in which the chemical phenomena take place in man, and have endeavoured to preserve, as far as possible, their actual form; but we have been unable to represent the relative positions they occupy in the body, where they are dovetailed into and cover each other.

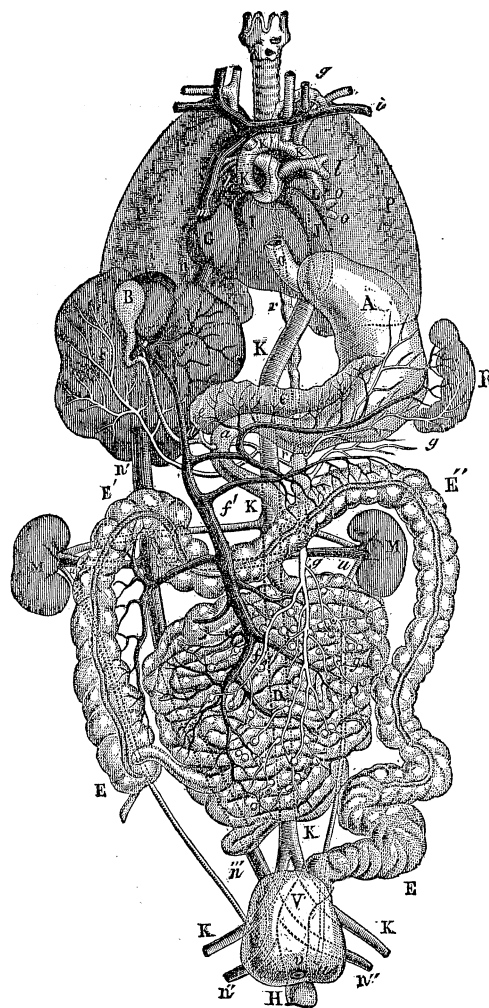


Fig. 686.

## DIGESTION.

§ 1668. The object of digestion is to modify, disaggregate, and dissolve alimentary substances, in order to enable them to pass subsequently into the general circulation.

The various acts of the function of digestion are as follows:

From the mouth, where the food is chewed by the *teeth* and moistened with saliva, it is conveyed into the stomach A, passing through the oesophagus O. The function of the saliva is chiefly

physical, and assists the mastication and deglutition of food. The saliva may, however, act chemically, by effecting the transformation of the starch into dextrin and glucose; the latter action being probably very limited, because at a later period the food comes into contact with several other juices which effect the same transformation.

Having reached the stomach A, the food is subjected to the action of a special juice, called *gastric*, secreted by the parietes of the stomach, and furnished by peculiar vessels belonging to the sanguine circulation. The gastric juice modifies, dissolves, or *digests* only the nitrogenous alimentary principles, such as the albumen, fibrin, casein, without in any way altering the fatty substances, and merely producing the hydration of the amylaceous matter.

When the food has remained for some time in the stomach A, it leaves it, impregnated with gastric juice, and passes into the *duodenum a*, where it first meets with the bile, brought from the *gall-bladder B* and liver F, by the *duct cd*, called *ductus choledochus*. The action of the bile on food is not well known, and some physiologists even believe it to act no part in the phenomena of digestion, and consider it as merely an *excrementary fluid*.

§ 1669. In the duodenum the food is moistened, not only by the bile, but also by the *pancreatic juice*, supplied to the duodenum by the *pancreatic duct, e*, which juice is produced in a peculiar organ, the *pancreas C*, where it is extracted from the fluids carried into the latter by the circulation. The pancreatic juice acts, *instantaneously*, on the non-nitrogenous alimentary substances, converting the fecula into glucose, and the fatty matters into an emulsion, which renders them fit for absorption.

§ 1670. The alimentary substances, modified by the successive influence of the gastric juice, bile, and pancreatic juice, pass from the duodenum *a* into the small intestine D, D, ... a tube of considerable size, extending from the duodenum to the *cæcum E*, which itself communicates with the large intestine EE'E''E'''. The extremely long parietes of the small intestine chiefly effect the absorption of the digested food and its passage into the circulation. The alimentary substances which reach the intestine in a condition to be absorbed, are of two kinds: 1st. Nitrogenous substances, dissolved by the gastric juice, and amylaceous substances, converted into dextrin and sugar by the action of the saliva and the pancreatic juice; and, 2d. The fatty substances which have been made into an emulsion, by the pancreatic juice, without being dissolved.

A special system of absorbent vessels, terminating in the small intestine, is contrived for each of these peculiar conditions of the absorbable alimentary substances: 1st. The system of the *vena porta ff'ff'*, which absorbs the nitrogenous and saccharine matters, and conveys them, with the venous blood of the intestines and the spleen R, into the liver F, where they undergo peculiar modifications, to pass thence in the *right auricle G* of the heart; and,



2d. The system of *chyliferous vessels*  $g, g, g$ , which absorbs only the fatty substances, and conducts them into the *left subclavian vein*  $i, i$ , to pass thence directly into the right auricle  $G$  of the heart, without traversing the liver. In the small intestine is effected the division between the digested alimentary substances, which are to be *absorbed* by the organism, and are called, on that account, *accrementitious substances*, and those which, remaining untouched, or having been insufficiently modified by the digestive fluids, are rejected externally, and consist of the *excrementitious substances* or *fæces*.

§ 1671. The dimensions and developments of the whole digestive apparatus, stomach, duodenum, and small intestine, vary greatly in different classes of animals: in the carnivorous, the food of which is much more easily dissolved by the gastric and pancreatic juices, they are relatively much less developed than in the herbivorous animals, of which the food, being highly charged with ligneous matter, dissolves with much greater difficulty.

§ 1672. The residue of the alimentary matter passes from the small into the large intestine  $EE'E''E'''$ , where it remains a greater or less length of time, and probably experiences new modifications and peculiar absorptions. It there acquires a disagreeable and peculiar odour, the cause of which is unknown, and is finally rejected, in the state of excrement, by the anus  $H$ .

#### CIRCULATION OF THE BLOOD.

§ 1673. We have followed the course of the alimentary matters through the *primæ viæ*, from their entrance at the mouth to the absorption of the digested portion into the general circulation, and the rejection of the residue by the anus. In following the new route of the digested portion, we shall find it ministering to the growth and renovation of the organs, to the production of juices essential to the chemical operations we have enumerated, and to the development of heat necessary to the animal, to be excreted, finally, either in gaseous compounds, with the gases of respiration, or in solution in the urine or sweat, or in forming peculiar fluids, such as milk, semen, etc.

After their absorption by the vena porta  $ff'f''$ , or by the chyliferous vessels  $g, g, g$ , the digested alimentary principles reach, by various routes, the general circulation, that is, the *right ventricle*  $I$  of the heart, where they are mixed with the venous blood, which arrives from all parts of the body through the *upper vena cava*  $mm'$  and the *lower*  $nn'n''$ , after having effected alimentation, and been subjected to the phenomena of respiration, etc., which shall presently be described. The instinctive contractions of the ventricle  $I$  drive all this mixture through the *pulmonary artery*  $W'l'$  into the lungs  $P, P$ , where it meets with air, and produces the phenomena of respiration. The blood, before reaching the lungs, has a deep brown colour, and is *venous blood*; while as soon as it comes into

contact with the air in the lungs, it turns of a bright red, and gives off the greater portion of the carbonic acid it contained, which is an essential product of the chemical reactions it experienced in its nutrient functions, replacing it with a certain quantity of oxygen, and thus constituting *arterial blood*, which returns to the *left ventricle J* of the heart through the *pulmonary veins o, o*. The heart impels it into the *aortic or arterial system K, K, K,...* to be distributed to all the organs of the body. The principal forces which effect this circulation appear to be the contractions of the left ventricle J, as well as the contractive forces of the arterial coats. If the arterial blood experiences chemical changes between leaving the heart and entering the organs, they are as yet unknown.

The arterial blood, after reaching the tissues of each organ, that is, after having entered the capillary circulation, experiences chemical modifications, differing in each organ. The oxygen which it had absorbed by contact with the air in the lungs, and which had effected its red colour, gradually disappears, producing the phenomena of oxidation, while it is replaced more or less completely by carbonic acid, which is one of the products of oxidation; the blood then receiving its brown colour, and becoming venous.

Arterial blood may be considered as of the same composition at the moment of entering each organ, which is not true of venous blood, the latter certainly undergoing special modifications in the various organs through which it passes, and which it nourishes. It is this blood, modified by the various functions it has fulfilled in the organs, which separates into two different liquids, venous blood properly so called, and *lymph*, both of which return to the right heart GI by special muscular systems, and are there mixed with the new liquids arising from digestion, to form a new blood, possessing all the necessary nutritive powers, and which again resumes the round of the circulation. The course of the blood from the right heart GI, to the left heart JL, passing through the capillary system of the lungs, is called the *lesser circulation*, while its return from the left heart to the right, passing through the capillary tissue of the organs of the body, is the *greater circulation*.

§1674. We have said that the *arterial* blood, passing through the capillary tissue of the organs, is chemically modified and converted into venous blood and *lymph*: now, it happens that while traversing certain capillary tissues, the blood gives out certain liquid or gaseous products. When the products, thus separated, are to be used for special purposes, they are called *secretions*; but when, on the contrary, they are to be rejected, they are termed *excretions*. The principal secretions are,

1st. The gastric juice, secreted by the stomach.

2d. The pancreatic juice, formed in the pancreas, whence it passes into the duodenum.

3d. The bile, produced in the liver, and accumulated in the gall-bladder.

4th. The intestinal juice, which appears to be secreted by the intestines, but is perhaps only an alteration of the foregoing digestive juices.

5th. The saliva, secreted in the mouth by the *salivary glands*.

6th. The semen of male animals, formed in the testes.

7th. Milk, secreted by the *mammary glands*, and collecting in the spongy tissue constituting the *mammæ*.

8th. The water of the amnios surrounding the foetus, in pregnant females.

Among the excretions, we distinguish,

1st. The sweat, excreted by peculiar glands, the *sudoriferous*, of which the orifices open on the surface of the skin.

2d. The urine which arises from a peculiar analysis of the arterial blood in passing, during the greater circulation, through the *kidneys* M, M, which analysis separates from it a liquid charged with mineral salts and highly oxygenated organic substances, such as urea and uric acid; which substances, being only the residue of chemical changes in the food, must be rejected. The urine is conveyed by special ducts, the *ureters uu'*, into the bladder V, where it collects, until the animal expels it by the urinary passages *v*.

3d. The gaseous products expelled by the act of respiration.

4th. Gases arising in greater or less quantity during the digestion of the food in the stomach or intestines, and which are emitted either from the mouth or from the anus.

#### RESPIRATION AND ANIMAL HEAT.

§ 1675. It has been long since considered as an established fact that the phenomenon of respiration consists in a combustion constantly taking place in the lungs, between a portion of the carbon and hydrogen of the blood, and the oxygen of the atmospheric air, which explains why arterial differs from venous blood by containing less carbon and hydrogen. Such, however, is not the theory now most received by physiologists. According to them, the venous blood, having reached the lungs, disengages carbonic acid, and absorbs oxygen, which it carries in a state of solution into the arterial system and the capillaries attached to it, the dissolved oxygen effecting in its course the oxidizing processes necessary to animal life, while the carbonic acid formed dissolves in the blood, and is disengaged only when the blood, having returned to the lungs, comes again in contact with the air. The exchange of the oxygen and carbonic acid is effected through the very delicate membrane which lines the air-cells of the lungs, and according to some, ensues merely in consequence of the ordinary laws of the solution of gases in liquids exposed to atmospheres of known composition, while others regard it as a special *endosmose* performed by the porous membrane. In all

cases, carbonic acid would no longer be formed solely in the lungs, but in all parts of the circulation.

The change of colour, so well marked and so instantaneous, of the venous blood by contact with the air, is not easily explained by a simple solution of oxygen gas; and it appears to us more probable that the oxygen forms, with certain substances in the blood, a true chemical compound, which again gives off its oxygen readily enough to effect instantaneously the oxidation of other substances. The carbonic acid produced by this oxidation in the capillaries would remain dissolved in the blood, on account of the high pressure to which the latter is subjected, which pressure must be admitted in order to explain the passage of so thick a fluid through such narrow tubes. The carbonic acid would be then more readily evolved when the blood reached the lungs, because it would there be subjected only to the ordinary pressure of the atmosphere.

§1676. We shall regard all the gases exhaled by the animal as products of respiration. They belong to three distinct orders of functions: the pulmonary respiration, cutaneous exhalation, and exhalation through the intestinal canal. In warm-blooded animals the second is much less active than the first, while in cold-blooded animals, on the contrary, it is equally, and perhaps more energetic; for example, in frogs, which can live for several days deprived of their lungs, by breathing through the skin; or in salamanders, which have lived for several months after the loss of their head, and the cicatrization of the wound. The ensemble of these functions is generally called by physiologists *perspiration*.

§1677. Warm-blooded animals, living on their ordinary food, always *exhale* nitrogen, but in very small quantities, since it rarely exceeds  $\frac{1}{10}$  of the weight of all the oxygen consumed by respiration. When these animals are in a state of inanition, there is frequently an *absorption* of nitrogen, the quantity absorbed being in proportions as small as that exhaled in the preceding case. It is very frequent in birds in a state of inanition, though rare in mammiferous animals. These alternations of absorption and exhalation of nitrogen lead us to believe that the two phenomena always occur simultaneously, while experiment only demonstrates the variable and always small result of their opposite effects, which then might be individually much greater than is supposed.

Cold-blooded animals also appear to exhale small quantities of nitrogen.

1678. The total quantity of oxygen which the animal takes from the air, in the act of respiration, is not always again found in the carbonic acid exhaled, a portion of the oxygen most frequently disappearing in other non-gaseous compounds, which remain in the animal economy, or are expelled from it with the excrementitious matters—principally with the urine. The ratio between the quantity of oxygen found in the carbonic acid and the whole quantity of

oxygen consumed, depends greatly on the nature of the food, and varies very little in animals living on the same aliments, though they may belong to very different species. The greatest absorption of oxygen in the state of non-gaseous compounds takes place when animals are fed on meat; the ratio between the weight of oxygen contained in the carbonic acid and the whole oxygen consumed, being then comprised between 0.67 and 0.74. This ratio is greater when animals are fed on vegetables; and in rabbits subjected to this regimen, it has varied from 0.85 to 0.95. It is still greater when animals are fed on bread or grain; for it may equal, and sometimes even exceed unity, so that the animal then evolves in the state of carbonic acid, a quantity of oxygen greater than that which it has taken from the atmospheric air, the excess of oxygen necessarily proceeding from the food. In a rabbit fed temporarily on bread and bran, the ratio between the oxygen contained in the carbonic acid exhaled and the whole quantity of oxygen consumed was 0.997; while in chickens fed on grain it varied from 0.90 to 1.03; and lastly, in animals absolutely dieted, the ratio was nearly the same as when they are fed on meat. In fact, the carbon furnished for respiration can, in this case, only arise from themselves, that act being then accomplished in them, as if they were carnivorous, even though they were birds which naturally feed on grain.

1679. In the mammiferæ and in birds, the quantity of carbonic acid formed by contact with the body, and which is disengaged by the intestinal canal, is always very small, since it rarely reaches  $\frac{1}{10}$  of that furnished by the pulmonary respiration. Small quantities of hydrogen and protocarburetted hydrogens traces of ammonia, and excessively small quantities of sulphuretted gases, are disengaged through the same passages. To recapitulate, in warm-blooded animals, the pulmonary respiration predominates so greatly over the secondary causes of exhalation and absorption which accompany it, that all the peculiarities which characterize it may be inferred from observations made on the whole respiration, as though it alone were active. On the contrary, in cold-blooded animals, the cutaneous respiration predominates to so great a degree that frogs have continued to breathe for several days when deprived of their lungs, nearly with the same energy, absorbing and evolving the same gases, in nearly the same proportion, as well as in nearly the same absolute quantities.

§ 1680. Hibernating animals, as the marmot, during their waking life, breathe precisely in the same manner as other animals, while the phenomenon is wholly changed during their sleep, their temperature then exceeding that of the surrounding medium only by a few degrees, and the consumption of oxygen being excessively feeble, and generally less than  $\frac{1}{30}$  of that required by the same animals when awake. Rather less than one-half of this oxygen only

is found in the carbonic acid exhaled, the balance being assimilated internally in the shape of non-gaseous compounds, and being probably partly used to form water, a small portion of which is lost by perspiration, on account of the low temperature of the animal. It hence follows that the weight of the carbonic acid exhaled is less than that of the oxygen absorbed, and the animal *increases in weight by perspiration*. This increase, however, does not take place continuously, for, every few days, the animal generally partially awakens and expels his urine. When the marmot fully awakes, his respiration becomes extremely active, much more so than when he has been awake for some time; and his temperature rises rapidly, while his limbs gradually lose their numbness, and the animal is seized with a violent shivering, caused by the sensation of cold, which he did not feel during sleep. The conditions of existence are no longer the same in the two states of the same animal. The waking marmot becomes asphyxiated, like the other mammiferæ, in an atmosphere poor in oxygen, while in the torpid state he would be unaffected by it. He cannot, however, bring himself voluntarily to this state, in order to continue to live in an atmosphere which his instinct tells him must prove fatal to him.

§ 1681. The respiration of animals does not appear to be changed in an atmosphere richer in oxygen than ordinary atmospheric air, nor even in pure oxygen; the same being true of an atmosphere containing a large proportion of carbonic acid, provided it contain also a sufficient quantity of oxygen. Lastly, if the nitrogen of our ordinary atmosphere be replaced by an equal volume of hydrogen, the animal breathes as usual, without any injurious effects.

§ 1682. The internal combustion of the carbon which serves to form carbonic acid is certainly one of the sources of animal heat. This fact is evident, not only as being a necessary consequence of the evolution of heat which always ensues on the combustion of carbon, either by active burning or in solutions, as in alcoholic fermentation, but is also manifested in the variations of respiration, according to circumstances, in maintaining the constancy of temperature. Thus, the quantity of oxygen consumed by the same animal, and the quantity of carbonic acid exhaled in equal periods, are the greater in proportion to the depression of the surrounding temperature; and it is also greater when the nitrogen of its artificial atmosphere is replaced by hydrogen, the relative refrigerating power of which is much greater. On this account, animals of the same class consume, in a given time, a quantity of oxygen in inverse ratio to their size; the loss of heat from the surface being proportionally much greater in the smaller than in the larger animal. For example, the consumption of oxygen for 100 gm. of substance is 10 times greater in sparrows than in fowls.

It has long since been admitted that the heat evolved by an animal in a given time is precisely equal to that which, by a vivid combustion

in oxygen, the carbon contained in the carbonic acid produced would afford, and the hydrogen which would form water with that portion of oxygen consumed, which is not found in the carbonic acid. It is highly probable that animal heat is wholly produced by chemical reactions ensuing in the economy; but the phenomenon is too complex to allow of its calculation from the quantity of oxygen consumed. The substances consumed by respiration generally consist of carbon, hydrogen, nitrogen, and oxygen, often in considerable proportion; and when they are completely destroyed by respiration, the oxygen they contain contributes to the formation of water and carbonic acid, and the heat evolved is necessarily very different from that which carbon and hydrogen, supposed to be free, would give off in burning. These substances, moreover, are never completely consumed; a portion being converted into other substances, which play special parts in the animal economy, or which escape in the excretions, in the state of highly oxidized matters, (urea, uric acid.) Now, in all these transformations and assimilations of substances in the organs, heat is evolved or absorbed; but the phenomena are evidently so complicated that we shall probably never be able to make them the subject of calculation.

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§ 1683. We shall now describe more in detail the principal properties and chemical composition of the liquids which are found in the animal economy.

#### BLOOD.

§ 1684. The blood is a liquid which circulates in the various parts of the animal economy, and furnishes the organs with the materials necessary for their life and growth. In vertebrated animals, such as man, the mammiferæ, birds, reptiles, and fishes, the blood is of a bright red colour; while in the invertebrata, as in insects, the crustaceæ, mollusks, and zoophytes, it is much more fluid and colourless, or merely tinged of a yellow, green, rose, or lilac hue. The blood is much denser and thicker in man and the warm-blooded animals, such as the mammiferæ and birds, than in cold-blooded animals; its density and viscosity varying according to the food and the more or less recent loss of blood which the animal may have sustained. In an adult man, the average density of the blood is 1.054 at 59°; being somewhat less in females, particularly during pregnancy, when it falls to 1.045.

Two kinds of blood are distinguished in man and warm-blooded animals: *arterial blood*, which is of a vermilion red, and *venous blood*, the colour of which is darker and of a brownish red, which peculiar colour is produced, as we have shown, (§ 1673,) by the action of the atmospheric oxygen on the blood; and it therefore exists only in animals which breathe in the air, and is not observed during intra-

uterine life. The colour of foetal blood is intermediate between that of the venous and arterial blood of adult age.

§ 1685. When fresh blood of a vertebrated animal is examined under the microscope, it is seen to be formed of a colourless, or nearly colourless liquid, in which red bodies, similar in form, and called *blood-globules*, are disseminated, which are characteristic of each genus of animals. They form in man and the greater part of the other mammiferæ small, circular, flattened disks; while in birds, reptiles, and fishes, they are elliptical. Their diameter in man is about  $\frac{1}{120}$  of a millimetre, being smaller in the majority of other mammiferæ, and in the goat attaining only about  $\frac{1}{200}$ . In birds, these globules are larger than in the mammiferæ; while they attain their greatest size in the family of the batrachians and reptiles: thus, in the blood of the frog, they are nearly  $\frac{1}{45}$  of a millimetre in length and  $\frac{1}{5}$  in breadth. Lastly, in fishes, the globules are intermediate in size, between those of birds and those of reptiles.

Fig. 687 represents the blood-globules of the frog, consisting of flattened elliptical disks, of which the central part, less coloured and protruding, is surrounded by a kind of deep-coloured border. Their anatomical study by the microscope and powerful chemical reagents shows them to be composed of two entirely distinct parts, a central nucleus and an envelope resembling a small bladder, containing a coloured gelatinous and very elastic substance. When any part of a frog, sufficiently thin to be translucent, such as the web of

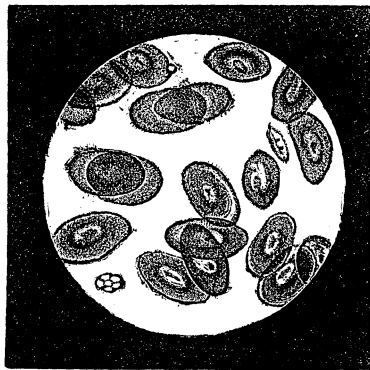


Fig. 687.

the foot or the tongue, is examined under the microscope, the globules will be seen to be rapidly carried through the capillaries with the watery fluid, and to be momentarily compressed in order to pass through the smallest tubes. Blood-globules may be preserved for a long time in their natural liquid; while, when water is added, they swell, probably in consequence of endosmose, and tend toward a spherical shape. The central nucleus does not appear to undergo any change. Certain acids, such as phosphoric, oxalic, citric, and acetic, rapidly dissolve the external envelope and expose the nucleus; while alkaline liquids dissolve the whole globule. The globules remain unchanged, and without any appreciable alteration of form, in a solution of sugar or gum, and in several saline solutions, such as those of nitrate of potassa or soda, and chloride of potassium and of sodium. Fig. 688 represents the globules of human blood, in which, as in the blood-globules of the other mammiferæ, the central portion is less projecting than the



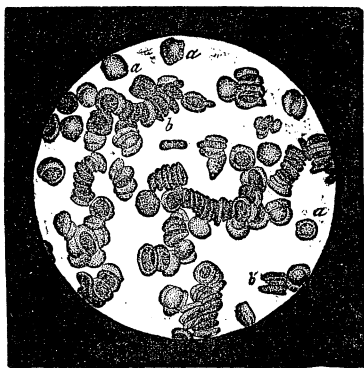


Fig. 688.

border, while the nucleus is not distinct, although we are led to admit the existence of one by analogy, and by the manner in which the globules are decomposed by chemical agents. In fig. 688 *a* is a front view of the globules, and *b* a profile view of the same.

In addition to the red globules which give colour to the blood, the microscope detects a very few colourless globules, of spherical form, closely resembling those seen in chyle, and some of which appear to be composed of fat alone.

The white or scarcely coloured globules in the blood of the invertebrata differ greatly from those of vertebrated animals, and their size varies in the same individual, while their form is generally spherical, and their surface is covered with asperities. No central nucleus can be distinguished.

§ 1686. The liquid surrounding the blood-globules of vertebrated animals is water, containing in solution a great number of different substances. The presence of albumen, fibrin, various fatty substances, some of which contain sulphur and phosphorus, a great number of salts, such as the chlorides of potassium and sodium, chlorohydrate of ammonia, the sulphates of soda and potassa, the phosphates of soda, lime, and magnesia, the carbonates of soda, lime, and magnesia, and of alkaline salts, formed by fatty acids and by lactic acid, have been detected in blood. This fluid contains also several gases in solution: oxygen, carbonic acid, and nitrogen, which arise from the action of the air in the lungs. It has a peculiar mawkish taste, characteristic in some animals, and always exerts a well-marked alkaline reaction, which appears to be an essential of its nature, for animal life ceases when, by direct injections, the blood can be made acid.

In a healthy man, 100 parts of blood contain, on an average, 79 parts of water, 1 part of mineral salts, 19 of albuminous substances, and some thousandths of fibrin, besides the red colouring matter known by the name of *hematosin*; which proportions vary greatly with the state of health. In the blood of birds, the relative quantity of water is generally somewhat smaller than in man, while it is greater in that of the batrachian reptiles and fishes. As much as 98 per cent. of water has been found in the blood of a frog.

§ 1687. Blood drawn from a vein soon loses its fluidity and *coagulates*; which generally commences in 5 or 10 minutes after its extraction, but is not complete until the lapse of 8 or 10 hours. A gelatinous matter forms, which thickens more and more, until, after a certain length of time, the blood separates into two portions: one,

fluid, yellowish and transparent, called the *serum*; and the other, gelatinous and elastic, of a deep red colour, and called the *clot*, *coagulum*, or *crassamentum of the blood*. The coagulation of blood is produced by the fibrin, which remains in solution so long as the blood is under the influence of vitality, but separates from it when it is removed from the animal economy, carrying with it the blood-globules, in the same way that soluble albumen, used for the clarification of a muddy liquor, carries down the corpuscles which exist in it, as soon as it is coagulated by heat. If, instead of allowing the blood to rest, it is beaten with rods, the fibrin still coagulates, and forms whitish and elastic filaments, which adhere to the rods, the blood-globules not being included, because they are detached by the agitation of the fluid. Defibrinated blood no longer coagulates. It is easy to demonstrate, on the blood of frogs, the globules of which are too large to pass through filtering-paper, that fibrin is really in solution in the serous liquid, and does not constitute any part of the globules, as was long supposed. It is sufficient to pour upon a filter, previously moistened, the blood of a frog, at the moment of its extraction, to show that a portion of the liquid passes through the filter before the commencement of coagulation; and after collecting this portion in a watch-glass, the microscope will exhibit in it, after a short time, a colourless clot, which may be made visible by collecting it on a needle. This experiment does not succeed in human blood; nor in that of other mammiferæ, because the fluid is more viscid and the globules are sufficiently small to pass through the paper.

The blood-globules are not uniformly distributed throughout the coagulum, but fall toward the lower part, while the upper strata generally contain but very few of them; in which case they contract still further, and form a sort of pellicle, called the *buffy coat* of the blood. By forcibly compressing the clot, the greater part of the liquid serum may be expressed from it.

Serum is a yellow, slightly viscid fluid, of a density ranging from 1.027 to 1.029: it has a slightly saline taste, and coagulates at about 168.8°, which property it owes to the albumen.

Several saline substances prevent the coagulation of the blood: as, for example, sulphate of soda, the chlorides of sodium and potassium, nitrate of potassa, borax, etc.; and the proportion of these salts must be about  $\frac{1}{3}$  of the weight of the blood. The dilute mineral acids also prevent the coagulation of blood, but impart to it an oily consistence. A temperature of 86° or 104° appears to be the most favourable for coagulation, while cold retards it considerably.

Healthy human venous blood yields

Coagulum .....	13.0
Serum.....	87.0
	<hr/> 100.0

Coagulum	{	Fibrin.....	0.30	}	13.00	
		Globules {	Hematosin .....			0.20
			Albuminous matter.....			12.50
Serum....	{	Water .....	79.00			
		Albumen.....	7.00			
		Fatty substances .....	0.06			
		Various salts with mineral bases.....	0.94			
					<hr/> 100.00	

§1688. Hematosin, or the red colouring matter of blood, has probably not yet been extracted in a state of purity, and has not been obtained crystallized. In order to obtain it, sulphuric acid is added, by small portions at a time, to blood previously defibrinated by beating; until, by the coagulation of the albuminous substances, the liquid becomes like a thick broth of a brown colour. This mass being diluted in a small quantity of alcohol, filtered through muslin, and compressed, the residue is treated several times with alcohol acidulated with a small quantity of sulphuric acid, until the liquid has lost its colour, and the albuminous matter is thus almost completely bleached. The alcoholic liquor is supersaturated by ammonia, and then evaporated to dryness; when the residue, which is composed of hematosin, mixed with some fatty and some alkaline substances, is treated successively by ether, alcohol, and water, which dissolve the foreign substances and leave the colouring matter. It is then purified by dissolving it in ammoniacal alcohol, and again separating it by evaporation; the hematosin remains in the form of a blackish-red amorphous mass, which is tasteless and inodorous, and insoluble, when cold, in alcohol, water, or ether; while it dissolves readily in alcoholic solutions of potassa, soda, and ammonia, which it colours intensely red. This substance contains as much as 10 per cent. of sesquioxide of iron, which appears essential to the existence of the globules.

§1689. The quantitative analysis of blood is very difficult, and no very accurate process is yet known; the following being that most generally adopted by physiologists:

The blood is first beaten with a brush, until the fibrin is separated as perfectly as possible, in whitish filaments, which are carefully collected, and weighed, after being washed, on a cloth, with water, and then dried at 212° until the weight remains constant. Three or four times its volume of a saturated solution of sulphate of soda being added to the defibrinated liquid, in order to prevent the alteration of the globules, it is rapidly filtered, causing bubbles of air to pass constantly through the liquid in the filter, to prevent the globules from adhering to each other. In this particular case, the blood-globules do not pass through the filter, and the sulphate of soda prevents the coagulation of the small quantity of fibrin which may still remain in the liquid. The globules are washed with a

solution of sulphate of soda, dried in vacuo, and then treated successively with ether which dissolves the fatty matter, with alcohol which dissolves a small quantity of foreign organic matter, and with water which removes the sulphate of soda. The dried globules are insoluble in these various liquids, and undergo no change; and after being again dried, they are weighed.

This being done, another portion of the same blood is allowed to coagulate spontaneously, and the crassamentum being separated as completely as possible from the serum, they are weighed separately. The serum is then evaporated in a water-bath, and the residue dried at  $212^{\circ}$  or in vacuo, by which means is ascertained the proportion of dry substances and of water constituting the fluid. On the other hand, the crassamentum is perfectly dried at  $212^{\circ}$ , and its loss of weight is supposed to represent the water of the serum which was contained in the coagulum; when, by a proportion founded on the knowledge of the composition of the serum, above given, the weight of the serum contained and the weight of the solid parts of the serum which remained in the dried coagulum is ascertained. The latter weight, subtracted from that of the dried coagulum, represents the united weight of the fibrin and globules, which should be equal to the sum of the weights of the fibrin and globules obtained separately in the first analysis. The fatty substances are separated from the dried coagulum and from the residue of the evaporation of the serum by treating them with ether.

Lastly, the mineral salts are obtained by incinerating separately the coagulum and dried serum, and ascertaining the weight of the ashes, which may be then subjected to a special analysis, if a sufficient quantity of blood has been operated on. By subtracting the weight of the ashes and that of the fatty matter found in the serum from the weight of the dried serum, and taking into account the serum interposed in the coagulum, the weight of the albuminoid substances is obtained, added to a small quantity of other organic substances.

#### LYMPH.

§ 1690. Lymph is a liquid brought from all the organs of the body, by a system of vessels called *lymphatic*. It is a limpid, slightly viscid fluid, having an alkaline reaction, and coagulating spontaneously like blood. Its composition resembles that of fluid blood, with the exception of the coloured corpuscles; while fibrin, albumen, and the saline substances peculiar to blood are also found in lymph.

The lymphatic vessels which convey the lymph from the intestines, perform, during digestion, the function of absorbing the fatty matters; in consequence of which the lymph at this time acquires an opaline and whitish tinge, resembling milk. The name of *chyle* is given to this mixture of intestinal lymph with the fatty matter,

and the lymphatics of the intestine have received the name of *chyliferous* or *lacteal vessels*, from their function of conveying the white chyle.

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#### LIQUIDS WHICH APPEAR TO PLAY A PART IN DIGESTION.

§ 1691. Various liquids occur in the intestinal canal of animals, secreted by special organs enumerated § 1667 *et seq.*, and the principal duty of which appears to be to effect the solution of alimentary substances and their passage into the blood. Physiologists divide them into

- 1st. Saliva.
- 2d. Gastric juice.
- 3d. Bile.
- 4th. Pancreatic juice.
- 5th. Intestinal juice.

As the chemical nature of these various fluids is far from being precisely ascertained, we shall confine ourselves to the most general information on the subject.

#### SALIVA.

§ 1692. Saliva, the liquid which moistens the mouth, is secreted by peculiar glands, called *salivary*, in various quantities, according to the wants of the animal; the fluid being introduced most abundantly into the mouth during mastication, while its chief function appears to be to assist deglutition. The saliva, as it exudes from the mouth, is a ropy and opaline fluid, which, when allowed to rest, separates into an upper clear and fluid portion, and a lower more viscid portion, in which swim filaments of mucus and remains of organic substances. The density of saliva is but little greater than that of water, since it rarely exceeds 1.008, and its reaction is generally slightly alkaline. It precipitates several metallic solutions, and deposits, at the boiling point, some coagulated principles. Absolute alcohol precipitates from saliva a peculiar matter, called *ptyalin*, to which physiologists attribute a special function, because it converts starch into dextrin in a pretty short space of time, and subsequently into glucose; but this property is known to belong to all albuminous substances. To the saliva is attributed the formation of the deposits which adhere to the teeth, commonly called *dental tartar*, but which consist of earthy phosphates and carbonates, mixed with mucus and other organic substances which are as yet unknown.

#### GASTRIC JUICE.

§ 1693. The gastric juice is secreted by the parietes of the stomach, varying in quantity with that of the food to be digested; and its duty is to effect the solution of nitrogenous organic sub-

stances, for it appears to exert no action on fecula or fatty matters, since the latter leave the stomach without any remarkable change, and meet in the intestine only the fluids which, by affecting their solution or disaggregation, enable them to be absorbed.

When freed by filtration from certain mucilaginous substances and organic remains, gastric juice is a colourless and limpid fluid, having a saline taste, and a feeble but peculiar odour, which varies in different animals; and it always exerts a decided acid reaction on litmus. It may be preserved unchanged for an indefinite length of time in the air, and without losing the property of effecting the solution of nitrogenous alimentary substances. The essential constituents of gastric juice are alkaline salts, certain organic substances, and a free acid; the whole being dissolved in a large quantity of water, which forms 98 or 99 per cent. of the juice. The salts of gastric juice are chiefly alkaline chlorides and sulphates, in which soda predominates, the phosphates being found only in a very small proportion. In addition, small quantities of sulphate, carbonate, and phosphate of lime are also met with.

Gastric juice is divided into two organic compounds: a mucilaginous substance, the nature and functions of which are not determined, and a special nitrogenous substance, to which the greatest share in the phenomenon of digestion is attributed, known by the names of *chymosin*, *pepsin*, and *gasterase*. It may be precipitated from gastric juice by alcohol and acetate of lead, or may be separated by evaporation, it being in both cases obtained in an amorphous form, from which it is impossible to decide whether it is a simple and definite substance.

The acidity of gastric juice appears to be always due to the presence of a small quantity of free lactic acid.

When meat, cut into thin slices, is dipped into gastric juice, it is seen, at first, to swell and become translucent, after which it gradually disaggregates, and finally is wholly dissolved. From this powerful action we might be led to suppose that gastric juice would act on the coats of the stomach; but they are covered by a mucus, which is constantly renewed, and preserves them from contact with the juice; while, after death, this mucus becomes putrid, and the gastric juice then attacks the coats of the stomach.

#### BILE.

§ 1694. Bile is a liquid secreted by the liver, and collected in a special receptacle, the *gall-bladder*, placed immediately below the secreting organ.

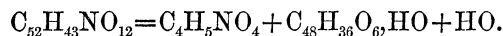
Bile is a ropy fluid, in man of a yellowish-green colour, of a brownish-green in the ox, and of an emerald-green in birds, amphibious animals, and fishes. It has a peculiar nauseous smell and a bitter taste. When poured into water, it first falls to the bottom of the fluid, but dissolves, on stirring, almost wholly, forming a

VOL. II.—3 N

frothy liquor. The reaction exerted by bile on organic colouring matters is not constant: it is frequently alkaline, sometimes neutral, and sometimes sensibly acid. Bile soon undergoes a change in the air, and putrefies, emitting a very disagreeable odour; and it coagulates by boiling. Acids effect a copious precipitate in it.

Although bile has been studied by a great number of chemists, they are not yet determined as to its nature, owing to the great mobility of its constituent principles in the presence of chemical agents.

Bile may be considered as a soap, with soda for its base, and formed by two acids, called *cholic* and *choleic*, and containing, in addition, small quantities of a crystallizable fatty substance, or *cholesterin*, fatty acids, and various salts, of which potassa, soda, ammonia, and magnesia, form the bases. The formula of cholic acid, which constitutes the greater portion of bile, is  $C_{52}H_{43}NO_{12}$ ; and by being boiled with caustic potassa, it is converted into glycocoll  $C_4H_5NO_4$ , and a new acid, called *cholalic*,  $C_{48}H_{36}O_6$ , HO:



But if the boiling be prolonged for some time, the cholalic acid is itself converted into a substance of a resinous appearance, *dyslysin*, to which the formula  $C_{48}H_{36}O_6, 2HO$  has been assigned. The following equation represents the final reaction:



Cholalic acid crystallizes readily in alcohol or in ether, the formula of its crystals being  $C_{48}H_{36}O_6, HO + 5HO$ . They are scarcely soluble in cold water, while they dissolve readily in solutions of the caustic alkalies and alkaline carbonates, but the salts thus formed do not crystallize by evaporation. If, on the contrary, an alcoholic solution of cholalic acid be neutralized by potassa, and ether added to it, colourless needles of cholalate of potassa  $KO, C_{48}H_{36}O_6$  are deposited. At a temperature of  $392^\circ$ , crystallized cholalic acid  $C_{48}H_{36}O_6, HO + 5HO$  is converted into a new acid, *choloidic*  $C_{48}H_{36}O_6, 3HO$ ; and if it be heated to  $570^\circ$ , it is changed into dyslysin  $C_{48}H_{36}O_6, 2HO$ ; water only being parted with during these successive changes.

The second acid of bile, or *choleic* acid, which contains a large amount of sulphur, has hitherto not been obtained in a state of purity. Boiling alkaline solutions convert it into cholalic acid and a neutral sulphuretted substance, *taurin*  $C_4H_7NS_2O_6$ , remarkable for its beautiful crystalline forms. Taurin is also formed by boiling bile with chlorohydric acid. It is a substance very soluble in boiling water, but nearly insoluble in absolute alcohol, and exerting no action on coloured reagents.

*Biliary Calculi, and Cholesterin*  $C_{25}H_{42}O$ .

§1695. Concretions of diversified forms and size, called *biliary calculi*, are frequently developed in the gall-bladder and biliary ducts. They are essentially composed of a fatty, crystallizable substance, *cholesterin*, mixed with substances of a resinous appearance and mucus. When the powdered calculi are treated with boiling alcohol, and the liquid is bleached by animal black, beautiful crystalline, brilliant, and colourless lamellæ of cholesterin separate on cooling. It is a neutral, insipid, and inodorous substance, slightly soluble in cold, and very soluble in boiling alcohol. It melts at  $278.6^{\circ}$ , being decomposed only at a very high temperature, and it resists the action of alkaline lixivæ.

Cholesterin is deposited from its alcoholic solutions in the state of hydrated cholesterin, which loses all its water at  $212^{\circ}$ . The composition of dried cholesterin corresponds to  $C_{25}H_{42}O$ , but its true formula cannot be exactly determined, for no definite compound of it is known. Chlorine forms products of substitution with it, its action stopping at *quadrichlorinated cholesterin*  $C_{25}H_{13}Cl_4O$ .

## PANCREATIC JUICE.

§1696. The functions of the pancreatic juice appear to be to effect the disaggregation of fatty substances, and to enable them to pass into the circulation, (§1669.) In fact, by mixing, at the temperature of  $100^{\circ}$  or  $104^{\circ}$ , (which is that of warm-blooded animals,) pancreatic juice with oil, butter, or fat, these substances are rapidly converted into an emulsion, and yield a whitish and creamy fluid; being, moreover, chemically altered and separated into fatty acids and glycerin. Of all the various fluids in the animal economy, pancreatic juice is the only one which exerts this remarkable action on fats.

Pancreatic juice is a colourless, adhesive fluid, which becomes frothy by shaking, and constantly displays an alkaline reaction. Heat coagulates it completely into a single mass, in which respect it closely resembles white of egg, but differs from it in many special properties. If alcohol be poured into pancreatic juice, the active coagulated principle is precipitated, but is wholly redissolved in cold water, even after desiccation, while the white of egg, when coagulated by alcohol, is insoluble in water. In addition to the organic substances, pancreatic juice contains alkaline carbonates and chlorides, and some few phosphates; the predominating base being soda.

## INTESTINAL JUICE.

§1697. The name of *intestinal juice* is given to a fluid secreted by the intestinal canal, and to which the liquefaction of amylaceous and ligneous substances is partly attributed; but the juice has hitherto not been obtained separately, being always mixed with other diges-



tive juices. The mixture exhibits sometimes an alkaline, sometimes an acid reaction, according to the nature of the food; but nothing accurate is known concerning its composition.

#### CHYLE.

§ 1698. *Chyle* is the fluid contained in the chyloferous vessels. When taken from the *thoracic duct*, which is the common trunk of these vessels, it is generally clouded and milky; its reaction being always alkaline. Its opacity is owing to the fatty matter which exists in it as an emulsion; and the microscope detects in it two kinds of colourless globules, some of which are fatty, while others constitute a peculiar substance, called *chyle-globules*, the shape of which is irregular.

When exposed to the air, chyle soon coagulates and divides into two portions: a colourless, or slightly reddish coagulum, and a colourless liquid, termed *serum of the chyle*; the fatty matter originally in suspension collecting on the surface of the serum. The coagulation of chyle, like that of the blood, is owing to the separation of the fibrin, which becomes insoluble, and carries with it other substances; while the serum chiefly contains albumen, which coagulates when the fluid is boiled. The relative proportions of the coagulum and serum are very variable, according to the species of animal, and, above all, according to the food. The chyle of a horse yields from 1.1 to 5.6 per cent. of fresh and from 0.2 to 1.7 of dried coagulum; while that of the dog yields from 1.3 to 5.7 of the same substance when moist, and from 0.2 to 0.6 when dried.

#### MILK.

§ 1699. Milk is a liquid secreted by special glands, called *mammary*, in the females of animals, after delivery. It is white and opaque, and serves as a type of all fluids of analogous appearance,

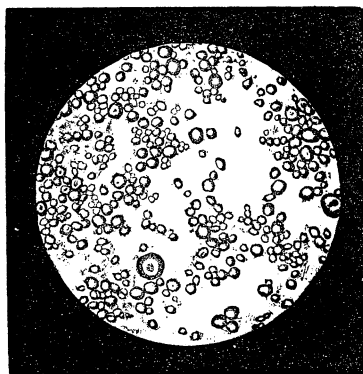


Fig. 689.

which are then said to be *milky*. The opacity of milk is owing to a multitude of small fatty globules, of from 1 to 3 hundredths of a millimetre in diameter, which are suspended in it in a state of emulsion. These globules are easily seen by examining a thin film of milk with a microscope, when they present the appearance represented in fig. 689. When milk is allowed to rest, the fatty globules, by virtue of their low specific gravity, rise to the surface, and form a coat of *cream*.

Ether does not remove the fatty globules by simply being shaken

with milk; while, if a few drops of acetic acid be added to it, and the liquid be then boiled, the globules unite, and may be dissolved by ether. If a concentrated solution of sulphate of soda or sea-salt be stirred in milk, and the whole then filtered, the globules are arrested, and the fluid which passes through is nearly transparent.

Milk contains, in addition to the fatty substance, a nitrogenous substance, which we shall describe under the name of *casein*, and to which it owes its principal nutrient qualities, a peculiar sugar, *sugar of milk*, albuminous substances, and mineral salts, all of which exist in it in different proportions, not only in the different species of animals, but even in the same individual. They depend greatly on the food, the greatest variations being found in the fatty matter, which does not exist in the same quantity at the beginning and end of the milking. The transparent part of milk, or *whey*, is much more constant, and is appreciably the same in the different periods of the same milking. The fatty globules, collected together, form *butter*.

Milk is habitually alkaline, but it soon sours in the air, particularly in warm or stormy weather, lactic acid being developed, which causes the coagulation of the casein. The caseous matter separates in clots, carrying with it the fatty globules; and the milk is then said to be *turned*. This change is avoided, without injuring the quality of the milk, by the addition of 2 or 3 thousandths of bicarbonate of soda; while the addition of a few drops of any acid will turn it. Fresh milk does not coagulate by boiling, but its surface becomes covered with white pellicles of an albuminous substance, which contains the fatty globules; and when the milk boils, these pellicles prevent the escape of the steam, causing the liquid to boil over if the vessel be not removed from the fire.

§ 1700. An accurate analysis of milk is a delicate operation, requiring a considerable length of time. The milk being evaporated to dryness in a porcelain capsule heated in a water-bath, the residue is dried at  $248^{\circ}$ , and weighed; the weight of the residue reaching 11 or 12 hundredths in cow's milk of good quality. It is treated with a mixture of alcohol and ether, which dissolves only the fatty matter; after which the latter, being separated, is evaporated and weighed. The casein, sugar of milk, and the salts remain in the residue after the treatment by alcohol and ether, and are weighed together after being dried, when the residue is incinerated, and yields the mineral salts, by subtracting the weight of which from that of the residue, the casein and sugar of milk are determined. The sugar is more accurately determined by optical experiments, for it possesses considerable rotatory power on the plane of polarization. For this purpose the rotatory power  $a$  of a certain weight  $p$  of sugar of milk, dissolved in 100 cubic centimetres of water, and observed in a tube 0.3 m. in length, being first ascertained, a certain quantity of fresh milk is heated to  $105^{\circ}$  or  $120^{\circ}$ , and treated with a few cubic

centimetres of acetic acid, which coagulates the casein and fatty matter. It is filtered, and some cubic centimetres of a solution of acetate of lead is added, which precipitates the albuminous substances, thus furnishing a perfectly limpid liquid after filtering. The rotatory power  $a'$  of this liquid in the tube of 0.3 m. in length being ascertained, the proportion  $x$  of sugar contained in it is then given by the proportion

$$a : a' :: p : x;$$

in which  $x$  does not represent exactly the proportion of sugar existing in 100 cubic centimetres of milk, because, before subjecting the liquor to optical examination, several liquids were added to the milk, while, if the quantity of the liquids added be exactly known, a correction can be made which furnishes the exact proportion of sugar in the milk subjected to analysis.

The casein is ascertained differentially.

§ 1701. The richness of various kinds of milk in fatty matters may be ascertained by a very simple experiment with a small instrument called a *lactoscope*; the experiment being founded on the fact that the degree of opacity of various kinds of milk, reduced to the same density, is very nearly in proportion to the quantity of fatty matter they contain in suspension. The lactoscope is a species of small opera-glass, formed by two plane glasses, which may be gradually brought into contact and separated by means of a very fine screw, the separation of the glasses being shown by a circular graduation marked on their rims. A small funnel at the upper part serves for the introduction of the milk between the glasses, while on the other side is the handle of the apparatus. When the glasses are in contact and the division marks 0, the milk is poured into the funnel, the glasses being separated by turning the movable mounting, while the milk falls between the glasses. The experimenter then stands before a candle at the distance of about 1 metre, and having brought the glasses together until the flame becomes distinctly visible, he gradually separates them until the exact moment at which the flame ceases to be visible. The relative richness in fatty matters of various samples of milk is given with sufficient accuracy by the degrees of separation of the glasses at the moment of the disappearance of the flame.

The mineral salts contained in 1000 parts of cow's milk have been found to consist of

Phosphate of lime .....	1.805
“       magnesia .....	0.170
“       iron .....	0.032
“       soda .....	0.225
Chloride of sodium .....	1.350
Carbonate of soda .....	0.115
	<hr/> 3.697

The analyses made of various kinds of milk have furnished, as an average, the following compositions :

	Cow.	Ass.	Goat.	Mare.	Bitch.	Human.
Water.....	87.4	90.5	82.0	89.6	66.3	88.6
Butter.....	4.0	1.4	4.5	trace	14.8	2.6
Sugar of milk and soluble salts.....	5.0	6.4	4.5	8.7	2.9	4.9
Casein, albumen, and insoluble salts.....	3.6	1.7	9.0	1.7	16.0	3.9
	100.0	100.0	100.0	100.0	100.0	100.0

§ 1702. The first milk furnished by the mammæ after delivery is called *colostrum*, and differs greatly in appearance from the milk which flows some days subsequently, being less fluid, exhibiting the consistence of serum, and showing a yellowish colour, while the microscope detects in it globules of fat, mucus, and irregularly shaped granules. To the colostrum are attributed purgative properties, which free the child from the meconium collected in its intestines.

*Sugar of Milk*  $C_{24}H_{42}O_{24}$ .

§ 1703. Sugar of milk, or *lactin*, is extracted by pouring into milk an acid which causes the coagulation of the casein, and then filtering and evaporating the liquid to the proper degree of concentration, when the latter gradually deposits sugar of milk, which forms semi-transparent and very hard crusts on the sides of the vessel. Sugar of milk is chiefly prepared in Switzerland, where the fluids which remain after the separation of the butter and casein are likewise used in making Gruyère cheese.

The taste of sugar of milk is sweet and agreeable, and milk owes its sweetness to it. It rotates toward the right. Heated to  $248^{\circ}$ , it loses 2 equiv. of water without melting, while at  $300^{\circ}$  it loses 3 equiv., and its composition is then represented by the formula  $C_{24}H_{19}O_{19}$ , which is also the case when it is combined with oxide of lead. Sugar of milk dissolves in 6 parts of cold, and 2 parts of boiling water, but is insoluble in alcohol and ether. Dilute acids convert it into glucose; while nitric acid, when heated with it, yields oxalic and mucic acids, the production of which latter distinguishes sugar of milk from the other sugars we have described. Sugar of milk undergoes alcoholic, lactic, or butyric fermentation, according to the nature of the ferment and the circumstances in which it is placed; the casein and albuminous substances producing these various fermentations. If fresh milk be maintained at a temperature of  $104^{\circ}$ , sugar of milk undergoes alcoholic fermentation, while if the milk be previously exposed to the air for some time, the casein is changed and produces lactic fermentation. It should be re-

marked that the elementary composition of lactic acid  $C_6H_5O_8, HO$  is the same as that of sugar of milk; and it may therefore be supposed, that in lactic fermentation the latter merely experiences an isomeric modification.

*Casein, or Caseum.*

§ 1704. In order to separate casein from milk, a certain quantity of sulphuric acid is added, which forms an insoluble compound with casein, precipitated in clots, and carrying with it the greater portion of the butyrous matter. The precipitate is collected on a filter and washed with distilled water, and then treated with a solution of carbonate of soda, which dissolves the caseous matter, forming a syrupy and cloudy liquor. If this be kept for some time at a temperature of  $68^\circ$  or  $77^\circ$ , the fatty substance forms a coat on the surface. The inferior aqueous liquid being drawn off by a siphon, and sulphuric acid added which again precipitates the casein, the latter is boiled with water to remove the sulphuric acid, when a portion of the casein is dissolved, which must be precipitated anew by carefully saturating the acid liquid with carbonate of soda. The casein is collected on a filter, washed with distilled water, and then, after being dried, with alcohol and ether, which dissolve the balance of the fatty substances. The casein is then considered as pure, although it possesses no character by which it may be ascertained to be a simple substance.

Casein is a white substance, resembling in appearance coagulated but pulverulent albumen. It is inodorous, tasteless, insoluble in water, alcohol, and ether, and always reddens litmus, although it is difficult to decide if this reaction be peculiar to it. It dissolves in alkaline liquids, from which acids precipitate it; and nearly all the acids precipitate it from milk, while the precipitate, which is a compound of casein with the acid, is redissolved in an excess of the latter acid. The sulphuric and chlorohydric compounds are less soluble, and when they are decomposed by the alkaline carbonates, or by that of lime or baryta, the casein dissolves and combines with a portion of the base.

*Manufacture of Butter.*

§ 1705. Butter which is merely the aggregation of the fatty globules of milk, is obtained from the cream which forms on the surface of this fluid when it is allowed to rest. The cream is poured into machines called *churns*, the forms of which vary in different countries; one of the best being a small barrel, having internally a dasher revolving on an axis. The dasher is rapidly turned, when the small fatty globules of the milk adhere to each other, and form, after some time, grains of butter, which separate from the watery fluid, or *buttermilk*, containing the casein, sugar of milk, and other soluble principles. The churn is then stopped, the

lid removed, and replaced by a covering of thin muslin stretched over wire-gauze. After churning slowly for a short time, nearly all the buttermilk flows out, and fresh water being substituted for it, the churn is again set in motion; which washings are repeated until the water comes out perfectly clear, when the butter is removed from the churn. Pure butter may be considered as a mixture of margarin, olein, and small quantities of butyryn, caprin, and caproin.

The excellence of butter depends not only on the quality of the milk, but also on its manufacture, since it is essential to use fresh cream, which can only be done on large farms, for in small ones it is necessary to save the cream of several days to have enough for a churning. Butter will keep longer when well freed from buttermilk, since the caseous and albuminous principles of the latter change first, and produce acid fermentations, which separate the butyric acid and other volatile acids, imparting to the butter a disagreeable, rancid taste. The decomposition of these substances is prevented by the addition of chloride of sodium, or by *salting the butter*.

#### *Manufacture of Cheese.*

§1706. Cheese is a mixture, in different proportions, of coagulated caseous matter and butter, and is generally prepared from skimmed milk, which has consequently lost the greater part of its fatty substances. When sufficiently compressed it is hard, translucent, yellowish, and possessing a greasy lustre, due to the butter it contains, and which may be easily separated from it by ether. The caseous matter separates in the form of cheese, when milk is left for some time, and at a slightly elevated temperature, in contact with the mucous membrane of the stomach of young calves, called *rennet*. The active principle of the rennet is called *chymosin*, but it has not yet been isolated with certainty, and nothing accurate is known concerning its manner of action. By maintaining the temperature at 77° or 86°, the caseous matter sets into mass, which is constantly agitated for some time until it becomes sufficiently solid; after which it is placed on a cloth, in a mould, and allowed to drain. If a hard cheese, and one that will keep for a long time is desired, the substance is pressed in the mould, so as to drive out the greater portion of the liquid. The cheeses are then laid on boards in a room, and left there for some time, their surface being frequently sprinkled with common salt.

The various kinds of cheese depend on the nature of the milk used in their manufacture, the proportion of cream left in it, and lastly, on the method employed for its manufacture.

## EXCRETIONS OF THE ANIMAL ECONOMY.

§ 1707. A great number of products, which have escaped assimilation, are rejected from the body of the animal. The water which existed in the food or drink, or that which was formed by the chemical reactions which take place in the animal economy, are expelled, either in the urine, or in the excrement or *fæces* of the intestinal canal, or by perspiration, or lastly, in the state of vapour, with the heated gases which escape from the air-passages in the act of respiration. The urine contains solid substances in solution, which arise from the various chemical reactions effected by vital action; while the excrements of the intestinal canal are composed of insoluble substances and substances in solution in water. Lastly, gases, called *intestinal*, frequently escape from the intestinal canal, which are formed in the chemical reactions ensuing in the stomach and intestines.

We shall successively describe,

1st. The urine of animals.

2d. The excrements, or *fæces*.

3d. The intestinal gases.

4th. The sweat.

5th. The gaseous products formed by the act of respiration.

The latter products having already been described, the first four only will occupy our attention.

## URINE.

§ 1708. The urine is formed from the blood, by an analysis of this fluid in the kidneys; and its composition varies in different animals, the difference depending chiefly on the food. In the carnivorous mammiferæ, the urine contains, in addition to mineral salts, albuminous and mucilaginous matter, and two substances of which we have not yet spoken, *urea* and *uric acid*. Urea often constitutes, of itself alone, more than one-half of the solid substances. The urine of herbivorous animals contains much less urea, while its place is occupied by a considerable quantity of a peculiar acid, called *hippuric*. The urine of all the mammiferæ in a state of inanition is similar, and resembles that of animals fed on meat, which might be expected, since the life of an animal in a state of inanition is supported at the expense of its own substance. Birds and fishes have no particular apparatus for the escape of the urine, which is voided with their excrement. The urine of the batrachians, of frogs for example, is very liquid, and contains only a trace of urea, while that of reptiles is nearly solid, and is chiefly composed of uric acid.

The quantity of urine voided by the same mammiferous animal varies with its food, and even changes with the same food, according to the surrounding temperature, a condition of repose or mo-

tion, and the pathological state of the subject. The volume of urine evacuated is in inverse proportion to the perspiration: thus, all other things being equal, the urine is more copious in winter than in summer, and in cold more so than in hot climates. The chemical composition of urine is not less variable in the same individual, that formed during digestion being always more rich in urea. On an average, an adult man forms, in 24 hours, 30 to 40 gm. of urea, which are evacuated with the urine.

We shall describe, with some minuteness, the principal organic substances found in the urine of animals, these substances being interesting, not only to the physiologist, but also to the chemist, since they assist in the production of many curious metamorphoses.

*Urea*  $C_2H_4N_2O_2$ .

§ 1709. Urea is obtained by evaporating fresh urine until it is reduced to  $\frac{1}{10}$  of its volume, allowing it to cool, and gradually adding nitric entirely free from nitrous acid, until no more precipitate is effected; when the urea thus forms a compound with the acid, nitrate of urea, which is very slightly soluble when cold, and is deposited in small coloured crystals. They are collected on a filter, washed with a small quantity of cold water, and, after being expressed between blotting-paper, are redissolved in boiling water, and the liquid boiled, for a few moments, with animal charcoal, deprived of its calcareous salts by chlorohydric acid; when the salt is again allowed to crystallize, by cooling. The nitrate of urea is obtained perfectly pure after several crystallizations, and is then decomposed by carbonate of baryta, which sets the urea free, and with the nitrate of baryta first formed remains in the liquid. The latter is evaporated to dryness, and the residue treated with boiling alcohol, which dissolves the urea alone, depositing it again on cooling, or by evaporation, in long prismatic crystals.

Urea may also be artificially produced by combining cyanic acid  $C_2NO, HO$  with ammonia  $NH_3$ ; the composition of cyanate of ammonia  $(NH_3, HO), C_2NO$  being identical with that of urea  $C_2H_4N_2O_2$ , and being, when left in water, immediately converted into its isomeric substance, urea. The following process, founded on the above, furnishes the means of obtaining large quantities of very pure urea: Cyanate of potassa is first formed, by heating to a nascent red-heat, in a retort, a mixture of 28 parts of dried prussiate of potash and 14 of binoxide of manganese, (§ 1504;) after which it is dissolved in water, treated with sulphate of ammonia, evaporated to dryness, and again treated with alcohol, which dissolves the cyanate of ammonia converted into urea, and leaves sulphate of potassa. The alcoholic liquor, when evaporated, yields beautiful crystals of urea.

Urea is a colourless, inodorous substance, of a fresh taste, very soluble in water, less so in alcohol, and almost insoluble in ether. Its solutions do not act upon litmus, although it combines with a

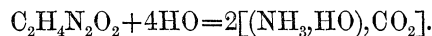


great number of acids, and forms crystallizable salts which exhibit the same rules of composition as the organic alkalies. There is, however, this difference between urea and the alkaloids, that it does not combine indiscriminately with all the acids: thus, it forms no compound with lactic acid, the acid properties of which are, nevertheless, well marked. It melts at  $248^{\circ}$  without change, being at a higher temperature decomposed into ammonia, which is disengaged, and into cyanuric acid, which remains in the retort; and if it be further heated, the cyanuric acid is converted into its isomeric modification, cyanic acid, which passes over in distillation. The urea is in this way separated into ammonia  $\text{NH}_3$ , and into cyanic acid  $\text{C}_2\text{NO}, \text{HO}$ ; and if these products are united in water, they again form urea. A certain quantity of urea is always formed in the neck of the retort, because the cyanic acid, at the moment of distillation, meets with the ammonia evolved during the first period of its decomposition.

Urea combines with several metallic oxides, particularly with the oxide of lead, which it dissolves; and it also forms definite and crystallizable compounds with chloride of sodium, chlorohydrate of ammonia, corrosive sublimate, nitrate of silver, and other substances. Hyponitric acid soon destroys urea, by decomposing it into carbonic acid and nitrogen, and moist chlorine produces the same effect.

Nitrate of mercury dissolved in nitric acid likewise decomposes urea, at the boiling point, into carbonic acid and nitrogen; and as the other components of urine do not disengage carbonic acid under the same circumstances, this reaction may be used for ascertaining very exactly the quantity of urea in a sample of urine, by collecting the carbonic acid in a weighed bulb-apparatus containing a concentrated solution of caustic potassa; the increase of weight of the apparatus, multiplied by the number 1.371, giving the weight of the urea.

A solution of urea, heated to  $284^{\circ}$  in a glass tube hermetically closed, is converted into carbonate of ammonia, by taking up the elements of 4 equiv. of water:



A prolonged ebullition with the caustic alkalies or mineral acids effects the same decomposition, which also ensues in urea dissolved in urine, when the latter is left to rest for several days; the albuminous substances contained in it exerting a special kind of fermentation on the urea. In consequence of this decomposition, putrefied urine is highly ammoniacal.

*Nitrate of urea* is formed by the direct combination of urea with nitric acid, and we have mentioned that it is precipitated in the form of small crystals when nitric acid is poured into a concentrated solution of urea. If heat be applied, the nitrate of urea crystallizes

on cooling in beautiful crystals, of the formula  $(C_2H_4N_2O_2,HO),NO_5$ , and which dissolve in 10 times their weight of cold water.

*Oxalate of urea* is still less soluble in cold water than the nitrate, and its formula is  $(C_2H_4N_2O_2,HO),C_2O_3$ .

Urea absorbs immediately chlorohydric acid gas, and is converted into the *chlorohydrate*  $C_2H_4N_2O_2,HCl$ , which is very soluble in water.

*Uric Acid*  $C_{10}H_4N_4O_6$ .

§ 1710. Healthy human urine generally contains 1 part of uric acid for every 30 parts of urea; which quantity may vary according to the food. Uric acid being very slightly soluble in water, is often deposited during the cooling of urine, in the form of small granular crystals, generally of a red colour. The excrement of birds and serpents contains very considerable quantities of it; and *guano*,\* which has been used during the last few years as a manure, and is merely the excrement of sea-birds, contains a large proportion of uric acid.

In the laboratory, uric acid is generally obtained from the excrement of the boa serpent. The powdered excrement being heated with a solution of potassa, which dissolves the uric acid and some other substances, the liquid is filtered and an excess of chlorohydric acid added, when the uric acid is almost wholly precipitated, since it requires about 1000 parts of water for solution. The acid is purified by dissolving it several times in alkalies and precipitating it by chlorohydric acid.

Pure uric acid forms small crystalline lamellæ, white, soft to the touch, inodorous, and tasteless: it feebly reddens litmus, and combines with all bases, the alkaline urates alone being soluble. The acid is insoluble in alcohol and ether.

§ 1711. Oxidizing reagents decompose uric acid in a very remarkable manner, producing many new substances, of which we can here only give a superficial description.

By heating water containing uric acid in suspension with bin-oxide of lead, the uric acid dissolves with a copious evolution of car-

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\* Bunzen gives the following as the average composition of the finer qualities of guano:

Urate of ammonia.....	9.0
Oxalate of ammonia.....	10.6
Oxalate of lime.....	7.0
Phosphate of ammonia.....	6.0
Double phosphate of magnesia and ammonia.....	2.6
Sulphate of potassa.....	5.5
Sulphate of soda.....	3.8
Chlorohydrate of ammonia.....	4.2
Phosphate of lime.....	14.3
Clay and sand.....	1.7
Water and undeterminable organic substances.....	35.3
	<hr/> 100.0

The result is calculated from numerous analyses of different kinds of guano, made by various chemists.—*W. L. F.*

VOL. II.—3 O

bonic acid, and the liquid deposits, on cooling, a neutral substance  $C_4H_3N_2O_3$ , which has already been found in the liquor amnii of the cow, and named *allantoin*. It crystallizes in white prisms, much more soluble in boiling than in cold water, and, when heated with nitric acid, it yields a considerable quantity of nitrate of urea; while it forms chlorohydrate of urea with chlorohydric acid; a peculiar acid  $C_{10}H_7N_4O_9$ , called *allanturic*, being formed simultaneously in both cases, which is also produced when uric acid or allantoin is boiled with water and binoxide of lead.

If uric acid be heated with 4 times its weight of nitric acid of the density 1.4, the former dissolves with effervescence, and the liquid deposits, on cooling, a crystallized substance, *alloxan*  $C_8H_4N_2O_{10}$ , which reddens litmus. This substance, treated when cold by alkalis, is converted into an acid  $C_4HNO_4$ , called *alloxanic*, which crystallizes in aciculæ, and forms perfectly well-defined salts. The alloxanate of baryta, which may be directly prepared by heating to  $140^\circ$  a mixture of alloxan and an excess of baryta, is decomposed at the boiling point into carbonate of baryta and a new salt of baryta, *mesoxalate of baryta*  $2BaO, C_3O_4$ , from which the mesoxalic acid may be separated by sulphuric acid. The formula of crystallized mesoxalic acid is  $C_3O_4, 2HO$ ; its 2 equivalents of water being basic, and the anhydrous acid, as it exists in the salts, containing only carbon and oxygen.

Alloxanic acid alone, when boiled for some time with water, gives off carbonic acid, and is separated into two substances: *leucoturic acid*  $C_6H_3N_2O_6$ , which is almost wholly precipitated in small granular crystals during the cooling of the liquid; and *diffluan*  $C_6H_4N_2O_5$ , a neutral substance, highly soluble in water, but insoluble in absolute alcohol, and yielding alloxan when treated with nitric acid.

Lastly, when a solution of alloxan is boiled with an excess of ammonia, a yellow nitrogenous acid is formed, called *mycomelinic acid*  $C_{16}H_{10}N_8O_{10}$ , almost insoluble in cold and very slightly soluble in boiling water. It forms yellow salts with bases.

We have shown that by heating uric acid with 4 times its weight of nitric acid, alloxan  $C_8H_4N_2O_{10}$  is obtained; and if the quantity of nitric acid be doubled, and the action prolonged, or if the alloxan be heated with this acid, a new substance, *parabanic acid*  $C_6N_2O_4, 2HO$  is formed, which remains in solution, but is deposited by evaporation in colourless crystalline lamellæ. Parabanic acid heated with an excess of ammonia is converted into *oxaluric acid*  $C_6N_2H_3O_7, HO$  which is itself, by continued boiling with water, separated into oxalic acid and oxalate of urea.

By causing sulphurous acid and ammonia to act successively on alloxan, a new acid of a very complicated composition is produced, called *thionuric acid*  $C_8H_2N_3O_{14}S_2$ . For this purpose, cold sulphurous acid is added to a concentrated aqueous solution of alloxan, until the latter smells of the acid; after which it is saturated with carbonate

of ammonia, caustic ammonia is added, and the whole boiled, when the thionurate of ammonia crystallizes on cooling. By pouring acetate of lead into a solution of this salt, thionurate of lead is precipitated, which, when decomposed by sulfhydryc acid, yields free thionuric acid, crystallizing in small aciculæ which redden litmus.

If chlorohydric acid be added to a boiling solution of thionurate of ammonia, very fine silky needles of a new substance, *uramil*  $C_8H_6N_3O_6$ , are deposited, which, though very slightly soluble in hot water, and almost insoluble in cold water, dissolve readily in ammonia. The ammoniacal solution turns of a reddish-purple colour in the air, and then deposits green crystalline aciculæ of a metallic lustre. Nitric acid converts it into alloxan.

By adding sulphuric acid to a solution of thionurate of ammonia, we do not obtain uramil, but *uramilic acid*  $C_{16}H_{10}N_5O_{15}$ , which is deposited by evaporation in a water-bath in the form of prismatic crystals or silky aciculæ, much more soluble in hot than in cold water. Uramilic acid forms crystallizable salts with bases.

By treating uric acid with an aqueous solution of chlorine, or boiling it with 32 parts of water, and adding nitric acid by drops until the uric acid is dissolved, it is converted into a neutral substance, *alloxantin*  $C_8H_5N_2O_{10}$ , which is deposited by evaporation of the liquid in colourless or slightly yellowish crystals, turning red by contact with the air and in the presence of ammonia, and assuming a metallic lustre. Oxidizing reagents convert alloxantin into alloxan, and the former is also obtained by treating alloxan with reducing substances, particularly with sulfhydryc acid, protochloride of tin, or by zinc in the presence of chlorohydric acid.

When alloxan is converted into alloxantin by sulfhydryc acid, the liquid, by being boiled, still maintaining the current of sulfhydryc gas, furnishes a new acid, *dialuric acid*  $C_8H_4N_2O_8$ , which is deposited in crystals on cooling, and possesses active acid properties.

The majority of the products derived from uric acid produce, in the presence of ammonia, a neutral substance, *murexid*  $C_{12}H_6N_5O_6$ , remarkable for its beautiful rose colour. In order to prepare it readily, 1 part of alloxan and 27 parts of alloxantin are dissolved in boiling water, and when the liquid has cooled to  $158^\circ$ , carbonate of ammonia is added, but not in excess. The liquid then deposits crystals of murexid, which is but slightly soluble in water, while it turns it of an intense purple colour. Its crystals are red and display the greenish reflection of the wings of the Spanish fly; it is insoluble in alcohol and ether.

Murexid is decomposed by the alkalies and acids into several products, among which may be distinguished alloxan, alloxantin, and a new crystalline substance, *murexan*  $C_6H_4N_2O_5$ , crystallizing in small silky, colourless spangles, and nearly insoluble in water. When exposed to the air and ammoniacal vapours, it assumes a beautiful red colour, and is converted into murexid; exhibiting a phenomenon

analogous to that of colourless *orcein*, which under the same circumstances is converted into coloured orcein.

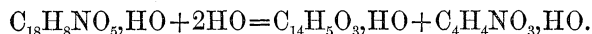
On evaporating rapidly by boiling a solution of alloxantin in chlorohydric acid, and allowing it to cool, the liquid deposits crystals of a new acid, called *allituristic acid*  $C_6H_2N_2O_3.HO$ . If dilute nitric be substituted for the chlorohydric acid, and the liquid be treated with sulphydric acid as soon as the alloxantin is dissolved, alloxan is deposited; and when the liquid is decanted and mixed with nitric acid it deposits an ammoniacal salt, formed by a new acid, called *dilituristic*, the composition of which is as yet unknown.

§ 1712. The rapid enumeration of the numerous products derived, thus far, from uric acid, proves very clearly the extreme mobility of certain organic molecular groupings.

*Hippuric Acid*  $C_{18}H_8NO_5.HO$ .

§ 1713. Hippuric acid exists in the urine of herbivorous animals and of young children. It is prepared by evaporating the fresh urine of a horse to  $\frac{1}{3}$  of its volume, and adding chlorohydric acid; when the liquid, on being left to itself, deposits coloured crystals of impure hippuric acid. They are redissolved in boiling water, when the liquid, after being bleached by animal charcoal, deposits white prismatic crystals of very pure hippuric acid, on cooling. Hippuric acid is much more soluble in hot than in cold water, and dissolves freely in alcohol, but is almost insoluble in ether; and it forms, with bases, salts remarkable for their beautiful crystalline forms. Under many circumstances, hippuric yields benzoic acid. When heated, it first melts, and is then decomposed, giving rise to cyanohydric acid, and a copious sublimation of benzoic acid, besides several other substances, the nature of which is not yet known.

If a solution of hippuric acid be boiled with powerful acids, the hippuric acid undergoes a very remarkable decomposition, already mentioned, (§ 1663,) being separated into glycocoll and benzoic acid:



Hippuric acid also furnishes benzoic acid when it is treated with oxidizing reagents, as, for example, by boiling its aqueous solution with brown oxide of lead, or with sulphuric acid and peroxide of manganese; carbonic acid being disengaged at the same time. Benzoic acid is also formed when it is heated with sulphuric acid at a temperature exceeding  $248^\circ$ .

Lastly, under the influence of certain ferments, hippuric acid is decomposed, and yields benzoic acid. These ferments naturally exist in the urine of herbivorous animals; and if the urine of a horse be allowed to become putrid, and be then concentrated by evaporation, a copious crystallization of benzoic acid is separated. This furnishes an economical method of preparing this acid, which

is also frequently found, ready formed, though in small quantities, in the urine of the herbivoræ.

Reciprocally, benzoic acid is readily converted, in the animal economy, into hippuric acid; and, after eating a small quantity of benzoic acid mixed with our food, we shall find a considerable quantity of hippuric acid in the urine arising from the digestion of this food. Healthy human urine almost always contains a very small quantity of hippuric acid.

#### ANALYSIS OF URINE.

§ 1714. The substances generally looked for in human urine are urea, uric acid, and the salts; the other principles, such as creatin, hippuric acid, and albuminous substances, generally existing in a quantity too small to allow of their accurate quantitative determination.

In order to obtain the urea, the urine is evaporated at a low temperature, and treated with alcohol, which dissolves the urea, together with a small quantity of unknown matter, while the uric acid, urates, and mineral salts remain in the residue. It is evaporated to dryness at a very gentle heat, and treated with a small quantity of dilute nitric acid, and again evaporated, when nitrate of urea remains and is weighed. It is, however, always to be feared that some of the urea may be destroyed during the evaporation, because a small quantity of nitrous acid may be formed by the reaction of foreign organic matters on nitric acid, and we have shown (§ 1709) that nitrous acid readily destroys urea. It is therefore much more exact to determine the urea by the quantity of carbonic acid which is evolved when a known weight of urine is decomposed by a mixed solution of nitrate and nitrite of mercury. (§ 1709.)

The uric acid is separated by pouring chlorohydric acid on the residue of urine which did not dissolve in the alcohol, and treating it with a sufficient quantity of weak alcohol, when the mineral salts are wholly dissolved, while the uric acid alone remains, and is weighed after desiccation.

The mineral salts are obtained by evaporating another portion of urine and incinerating the residue. The alteration which the original salts may have undergone by roasting must necessarily be taken into account.

We have said that urea forms more than one-half of the residue after the evaporation of the urine; and as this substance contains about one-third of its weight of nitrogen, the greater portion of the nitrogen of the food will be included in it. The proportion of urea and uric acid is much greater when animal food is used than when the subject feeds on vegetables.

§ 1715. In various diseases the urine is greatly changed, and renders the physician valuable assistance in the diagnosis of alterations which have taken place in the economy. In a peculiar disease

called *diabetes mellitus*, the urine is loaded with a considerable quantity of fermentable sugar, called *diabetic sugar*, which appears to be identical with glucose. Persons affected with this disease suffer constantly from thirst, drink largely, and pass considerable quantities of urine. The sugar is separated by evaporating the urine in a water-bath, and treating the residue with weak alcohol, which dissolves the saccharine matter. The liquid is bleached by animal charcoal, concentrated by evaporation to the consistence of syrup, and kept for a long time at a low temperature; when the sugar is deposited in the shape of little pyramids, which are washed with absolute alcohol, and purified by recrystallization.

The proportion of sugar in diabetic urine may be ascertained very exactly by optical experiments. (See note to page 478.)

#### CALCULI OF THE BLADDER.

§ 1716. Concretions, which sometimes attain a considerable size, are frequently found in the bladder, and are called *urinary* or *vesical calculi*. They are formed of very various substances, and are divided into,

1st. Calculi of uric acid, which are the most common, and are known by the physical and chemical properties of uric acid, particularly by that of dissolving in nitric acid, and producing a rose colour when the solution is evaporated in the presence of ammonia.

2d. Calculi of urate of ammonia, which exhibit, with nitric acid, the same phenomena as calculi of free uric acid, but which evolve, in addition, ammonia when they are heated with potassa.

3d. Calculi of phosphate of lime, which dissolve readily and without effervescence in dilute chlorohydric acid. By an excess of sesquioxide of iron added to the liquid, and then supersaturating it with perfectly caustic ammonia, the phosphoric acid is completely precipitated, in combination with the sesquioxide of iron, (§ 865,) while the lime remaining in solution may be precipitated by oxalate of ammonia.

4th. Calculi of a compound phosphate of magnesia and ammonia, which also dissolves readily in dilute chlorohydric acid. After having precipitated the phosphoric acid in combination with the sesquioxide of iron, as in the preceding calculi, carbonate or oxalate of ammonia is added, which precipitates the lime, if any be present, while the magnesia remains in solution, and may be separated by the processes indicated, (§ 592.) The ammonia is separated by heating another portion of the calculus with hydrated potassa. The majority of urinary calculi are complicated, being composed of a nucleus of uric acid of greater or less size, around which are formed concentric concretions of phosphate of lime and phosphate of magnesia and ammonia.

5th. Calculi of oxalate of lime, called also *mulberry calculi*, because their rugose and mamillated surface resembles that fruit.

They dissolve with difficulty in chlorohydric acid, but readily in concentrated nitric acid, which converts the oxalic into carbonic acid. The lime is separated by the processes indicated § 594. By heating these calculi with concentrated sulphuric acid, a gaseous, inflammable mixture of carbonic acid and oxide of carbon is disengaged.

6th. Calculi of *cystin*. These calculi are very rare, and are formed by a sulphuretted organic matter, easily recognised by its chemical properties.

Cystin is obtained in a state of purity by dissolving powdered cystic calculi in ammonia, filtering the solution, and then evaporating, when the cystin separates in small crystals, which do not retain the ammonia. The composition of cystin corresponds to the formula  $C_6H_6NO_4S_2$ , and it is a colourless, crystalline, inodorous substance, insoluble in water and in alcohol, but dissolving readily in ammonia. With the acids it plays the part of a weak base, readily dissolving in them, without forming fixed compounds.

## SWEAT.

§ 1717. Sweat is a liquid of acid reaction, which exudes from particular openings in the skin. It contains some unknown animal substances, and some mineral salts, among which have been found chloride of sodium, chlorohydrate of ammonia, the sulphates and phosphates of potassa and soda, phosphate of lime, and traces of oxide of iron.

## EXCREMENTS.

§ 1718. The excrements of mammiferous animals are composed chiefly of animal substances which have escaped liquefaction during their passage through the stomach and intestines, and contain, in addition, fatty matters, and several soluble and insoluble substances, the nature of which is unknown. In the newly-born infant, the intestinal canal contains a brown substance, called *meconium*, which the child voids during the few first days of extra-uterine life, the excrements soon changing when it is fed on milk. Meconium contains a considerable quantity of cholesterin, and a substance analogous to casein of milk.

Birds void their excrement and urine through the same canal, and they contain a large quantity of uric acid, besides some unknown substances.

## INTESTINAL GASES.

§ 1719. Gases are always evolved during digestion, their quantity varying with the food and the peculiar constitution of the individual. These gases are essentially composed of nitrogen, carbonic acid, hydrogen, carburetted hydrogen, and frequently of a small quantity of sulphydric acid. The proportions of the gases range between widely extended limits.



OF THE MANUFACTURE OF THE PRINCIPAL PRODUCTS  
OF ORGANIC ORIGIN, USED IN THE ARTS, OR IN DOMESTIC  
ECONOMY.

§ 1720. We shall close the present work by a brief account of the manufacture of the principal products, of organic origin, which are used in the arts, or in domestic economy. We shall, in this description, dwell only on the general chemical principles of these several manufactures, without touching upon the mechanical part, which is foreign to our subject, and would require details, the description of which would exceed our limits.

MANUFACTURE OF BREAD.

§ 1721. Bread is made from the *flour* of the cerealia, that is, from the product of the grinding of the grain, freed, by sifting or *bolting*, from the cortical portions, called *bran*. Bran still contains a considerable quantity of starch and nutritious matter, while the woody substance which constitutes the envelope of the grain, and which is of difficult digestion, exists in the proportion of about 8 hundredths; this proportion varying with the method of bolting.

Wheat-flour, which is the richest in gluten, is generally used in making bread, although, in countries where wheat cannot be grown, the inhabitants use barley or rye-flour, or mixtures of these cerealia, called *mestlin*, (*méteil*), which is obtained by sowing them together. A small quantity of rye-flour is often added to wheat-flour, in order to give the bread more flavour.

The following is the average composition of the principal wheat-flours consumed in France:

	Unbolted flour of native wheat.	Flour of hard wheat from Odessa.	Flour of soft wheat from Odessa.
Water.....	10.0.....	12.0.....	10.0
Dry gluten .....	11.0.....	14.6.....	12.0
Starch.....	71.0.....	57.6.....	63.3
Glucose.....	4.7.....	8.5.....	7.4
Dextrin.....	3.3.....	5.0.....	5.8
Bran .....	0.0.....	2.3.....	1.5
	100.0 .....	100.0 .....	100.0

§ 1722. The various processes in bread-making are mixing the flour with water, kneading, fermentation or rising, moulding it into loaves, and baking. By the first, the starch and gluten are moistened with water, and the soluble principles, such as dextrin, glucose, and the albuminous principles, dissolved; but as the paste, kneaded merely with water, would produce a hard bread, difficult of digestion, the light and puffy consistence seen in well-made bread

is imparted to the crumb through a ferment added to the paste, which acts on the dextrin and glucose, by effecting alcoholic fermentation. The gases which are disengaged during fermentation swell the paste, to which the gluten gives elasticity; and, if it be well made, all the small gaseous bubbles remain in the bread. The ferment is generally made by taking, at the close of each operation, a portion of the paste, and setting it aside for some time; when it is called *leaven* or *rising*. In large cities, or wherever breweries are found, a small quantity of beer-yeast is added to the rising to give it more activity; but the quantity must be carefully regulated, as too much would give a disagreeable flavour to the bread.

The following is the process adopted in the Paris bakeries:—The leaven being left, for 7 or 8 hours, in a gentle and uniform temperature, swells visibly and disengages an alcoholic odour, when it constitutes what is called *head-yeast*, (*levain de chef*.) It is kneaded with a quantity of water and flour sufficient to double its volume, still retaining the consistence of a firm paste, and is again allowed to rest for 6 hours. After this time, when the paste has become *levain de première*, an additional quantity of water and flour is added, and it is again mixed, the proportion of water being greater than in the previous operation; which process yields *levain de seconde*. Lastly, a similar addition is made to the *levain de seconde* as was made to the *levain de première*, the paste being carefully worked, and a *levain de tous points* obtained, the volume of which should be, in winter, nearly one-half of that of the dough intended for baking, and in summer only one-third. A certain quantity of salt is generally added, to heighten the flavour of the bread;  $\frac{1}{2}$  kilog. of salt being used for every 150 kilog. of flour, in the Paris bakeries.

The dough is then kneaded. The quantity of water necessary for the formation of the paste being first added to the rising, it is mixed for a long time, in order to obtain a perfectly homogeneous, fluid paste, to which the flour is gradually added, and which is then called the *sponge*. When the dough has been sufficiently worked, it is collected into a single mass, then again thoroughly worked by turning it in all directions, and finally let fall into the trough with its whole weight.

The kneading being terminated, the dough is divided into *loaves*, which are weighed to ascertain if they reach the legal standard, according to which 115 or 117 of dough should give 100 of baked bread. They are then dusted with flour or Indian corn meal, and placed on tables in front of the oven, to keep them at the proper temperature; when more active fermentation ensues, while the loaves gradually swell, until they have attained the proper size to be placed in the oven. The fermentation must not be too much prolonged, because it might degenerate into acetic fermentation, which would liquefy a portion of the gluten, and thus diminish the consistency of the dough.

The oven is generally of an elliptical form, and heated by wood or fagots of little value. The fuel should be properly distributed, in order to obtain a nearly uniform temperature; and bakers remove about 30 to 35 per cent. of the fuel in the state of *hot coals*. The proper temperature for baking bread is about  $570^{\circ}$ .

The largest loaves are first introduced, and then the smallest, which are placed in the front part, because they are to be first withdrawn; and the door is then closed. The heat dilates the gases, arrests the fermentation, vaporizes a portion of the water, and gives consistency to the gluten and amylaceous matter, which retain the shape they have assumed. The inside of the loaf, or *crumb*, does not attain a temperature above  $212^{\circ}$ , on account of the continual evolution of steam, while the outer portion, or *crust*, is completely dried, and has become torrefied by having reached a temperature of about  $400^{\circ}$ . Round loaves weighing 8 pounds remain about 60 minutes in the oven, and split loaves of 4 pounds from 36 to 40 minutes. When removed from the oven, they are laid upright, in order that they may not break before having acquired all their consistency, and at some distance from each other, that the vapours may pass off more easily.

The manufacture of bread has of late years been much assisted by the introduction of mechanical kneading and aërothermal ovens, which effect a more uniform baking.

#### BREWING.

§ 1723. Beer is an alcoholic beverage, made from the amylaceous substance of the cerealia, chiefly from barley, the price of which is lowest. The process of brewing may be divided into four distinct stages: 1. The *malting*, of which the object is to produce in the barley the principle which effects the conversion of starch into dextrin and glucose, and which essentially consists in causing the barley to sprout under the influence of a proper temperature and degree of moisture, diastase being formed at the origin of the sprouts, and in the succeeding operation converting the starch into soluble dextrin and glucose. 2. The preparation of the *wort*, (*moût*), or saccharification of the malt, which consists in treating the ground malt with water at a suitable temperature, in order to cause the diastase to act on the starch and dissolve the dextrin and glucose which result from this action. 3. The boiling with hops, which consists in heating the wort with hops in order to give it a peculiar taste and aroma. 4. Fermentation, which consists in mixing the cooled wort with a ferment, in order to effect the conversion of glucose into alcohol.

The barley is first placed in large vats of mason-work, with 4 times its volume of water, being stirred frequently to expel the bubbles of air between the grains, while those which arise on the surface, being generally defective, are skimmed off. The object of

this process is chiefly to swell the grains, in order that they may sprout more easily; and it lasts 24 or 36 hours in winter, during which time the water is renewed 3 times; while in summer it requires only 10 or 12 hours, but the water must be renewed 4 or 5 times.

The barley thus swollen is carried to the malt-house, a kind of cave or cellar, the floor of which must be kept scrupulously clean to avoid all injurious fermentations. Germination requires the assistance of moisture, air, and a temperature of from  $59^{\circ}$  to  $62^{\circ}$ , which conditions are most readily realized in spring or autumn; whence the name of *March beer* is given to that made in the spring, and is considered superior to that made in any other season. In the malt-house the barley is spread in a layer of about  $1\frac{1}{2}$  feet in depth, and thus left until it becomes heated; but when it begins to sprout, the thickness of the layer is reduced to 1 foot, and then to 3 inches when the germination approaches the proper point. It is also frequently stirred in order to renew the air in the interior of the layer. In the hot season, the germination is terminated in 10 or 12 days; while it requires 15 or 20 days toward the close of autumn, the sprout having then become  $\frac{3}{4}$  as long as the grain.

When the barley has properly sprouted, it is dried rapidly, in order to arrest the loss of the amylaceous matter which would ensue from a longer growth of the sprout and radicles. The drying is first made in the open air, by spreading the grain over the floor of a well-aired granary, and then in a stove traversed by a current of hot air, and called a *malt-kiln*. Desiccation renders the radicles of the barley very brittle, but they are easily removed by sifting them in a *winnowing-machine* or *fan*. The sprouted barley thus freed from the radicles is exposed for some time to the air, when it imbibes a small quantity of moisture, which facilitates its grinding. This operation is effected between horizontal stones, kept at such a distance from each other that the grain is broken and torn without being reduced to flour. The product is *malt*, which is stowed away for future use.

§ 1724. The saccharification of the malt is effected in large wooden vats, having a double bottom pierced with holes, intended to support the barley and facilitate the introduction and escape of the liquid. In the space between the two bottoms are the discharging-tube and one which conveys hot water. When the malt is placed in the vat, water at  $140^{\circ}$ , and equal in weight to  $1\frac{1}{2}$  times that of the malt, is poured in, the mixture being actively stirred with a kind of fork. It is then allowed to rest for  $\frac{1}{2}$  an hour, until the malt is thoroughly moistened, when water at  $196^{\circ}$  is added until the temperature of the mixture attains  $167^{\circ}$ , which is the most favourable for saccharification; after which it is again stirred, the vat covered, and the reaction allowed to continue for 3 hours. The saccharine fluid, or

*wort*, is then conveyed into a reservoir, and thence into the boilers intended for the decoction of hops.

As the first digestion with water only abstracts from the malt 0.6 of the saccharine matter it can furnish, an additional quantity of water at  $176^{\circ}$  is added, equal to one-half of that used in the first operation, and is allowed to act for 1 hour, the liquid produced being added to the first. Lastly, the malt is exhausted by water at  $212^{\circ}$ , and a liquid obtained which is used in making small-beer. The exhausted malt\* is used as food for animals.

The wort is heated to ebullition with hops in boilers, which must be kept covered to prevent the escape of the essential oil to which beer owes its aroma, and are furnished with an apparatus which constantly stirs the mixture. The strength of the wort is sometimes increased by the addition of glucose, (§ 1306,) molasses, or raw sugar. The wort thus hopped is conveyed into reservoirs, where it is clarified by rest, and then run off into other reservoirs, where it is cooled as rapidly as possible, by allowing the liquid layer only a thickness of 4 or 5 inches; the cooling vats being placed in large rooms surrounded by Venetian blinds, in order to afford a free circulation of air. The proportion of hops is about 1 kilog. for every hectolitre of table-beer, and 2 kilog. for every hectolitre of strong-beer.

When the wort is cooled, it is poured into a *fermenting vat* or *tun*, and a quantity of yeast added, varying, according to the season and strength of the wort, from 2 to 4 kilog. for every 1000 litres, and maintained at a temperature of about  $68^{\circ}$ . The fermenting-house should be well aired, in order to allow the carbonic acid to pass off rapidly. The fermentation lasts from 24 to 48 hours, producing a large quantity of froth, which falls from the tun into spouts arranged for the purpose, and which, when collected and expressed in bags, constitutes *beer-yeast*.

The tuns are always kept full by adding the liquid separated from the froth. The fermentation of table-beer is completed in small casks filled to the bung, and placed on a scaffolding over a spout which carries off the froth still arising from the liquor; and when the fermentation is finished the kegs are plugged, and the beer only requires a clarification with fish-glue.

Strong-beer is allowed to ferment slowly for several weeks after the fermentation in the tun, in large vats, holding as much as 2600 gallons.

#### CIDER AND PERRY.

§ 1725. An alcoholic liquor, called *cider*, is prepared from apples, and constitutes almost the sole drink in Normandy and Picardy; while pears yield a similar beverage, called *perry*. In the making of cider, a certain quantity of pears is often added to the apples, to give the liquor a higher flavour.

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\* Called, in this country, *grains*.—TRANS.

In order to make cider, the apples are crushed in a vertical mill, turning in a stone trough, with a pressure not great enough to mash the seeds, which would injure the flavour of the cider. About 10 or 15 per cent. of water is generally added. The mashed apples being put into heaps, and left for 24 hours, the cellular-tissue begins to separate, and fermentation develops a peculiar colouring matter, which gives cider its yellow tinge. After this maceration, the pulp is pressed, and 500 kilog. of juice are generally extracted from 1000 kilog. of apples. The apple-mash is again ground, after the addition of about 250 litres of water, and expressed; the liquid thus obtained yields cider of an inferior quality.

The apple-juice is allowed to ferment in vats or barrels, where it is freed from various substances, which are either deposited or float on the surface in the shape of froth. It is drawn off into large hogsheads, which are but loosely corked, in order to give exit to the carbonic acid generated during fermentation. During this second stage of fermentation, the cider retains a sweet taste, much admired by some persons; but in countries where cider is the general beverage, fermentation is allowed to continue to its completion, by which the liquor acquires an acid and slightly bitter taste.

## WINE-MAKING.

§ 1726. Grapes contain extremely numerous proximate principles: cellulose, pectin and its congeners, (§ 1296,) grape-sugar, tannin, albuminous substances, yellow, blue, and red colouring matters, fatty substances, tartrates of potassa and lime, silica, oxide of iron, etc. etc. Wine derives its alcohol from glucose; while the colouring matters and tannin, which exist chiefly in the skin of the fruit and the grape-stems or stalk, impart different shades to the various wines, according as one or other of the colouring principles predominates. These principles are not all equally fixed; the blue colour changing first, while violet-coloured wines become more red with age, and acquire a yellowish tinge when they are very old, because the red principle is destroyed before the yellow.

In wine-making, the grapes are, in the first place, pressed, most frequently by the feet of men, who walk about in the vat. In the manufacture of white wine, the pulp alone is pressed; while, if red wine is to be made, the pulp is left for several days to itself, to allow fermentation to take place, and the liquor to dissolve the colouring matters and tannin of the skins of the fruit and of the stalks. The pressing is frequently repeated, when the tissues are partly broken up by fermentation; but this is an operation requiring caution, as the carbonic acid, which is copiously evolved, might asphyxiate the workmen. For wines of superior quality, a partial picking is often performed, that is to say, a portion of the stalks are removed, when the latter are too abundant, as is the case in years when grapes are not very plenty. The vats in which the first fermentation is

effected are left open, though it would probably be better to keep them closed, in order to avoid the contact of air, which often produces acetic fermentation in the scum collected on the surface. The duration of the fermentation varies with the temperature and nature of the grape, and is known to be terminated by the almost complete cessation of the evolution of gas, and the colour of the wine, which contains a sufficient quantity of the colouring matter. For ordinary wines, it lasts from 3 to 8 days; while in some localities it is continued for a month or six weeks, the vats being then closed after the eighth day.

When fermentation has ceased, the clear liquid is drawn off by a stopcock, and the *must* is expressed; the latter being generally diluted with a small quantity of water, and again subjected to pressure, yielding a very weak wine, called *piquette*, which soon turns sour. The wine which flows spontaneously and that separated by compression of the pulp are generally mixed together, but are kept separate in the making of wines of superior quality, because that yielded by expression always contains some acid principles furnished by the stalks and seeds.

The wine is received into hogsheads, which are generally not closed, because fermentation goes on slowly, and carbonic acid is for a long time evolved. When this ceases, the wine is again drawn off, and, about the month of March or April, the fining is commenced.

Red wines are commonly fined with white of eggs, bullock's blood, or gelatin, which substances combine with the tannin and a portion of the colouring principle, and carry down, by coagulating, the substances in suspension which muddied the wine. To fine white wines, which contain but little tannin, it is necessary to use fish-glue, because it coagulates much more rapidly.

In bad years, when the grapes do not ripen perfectly, the quality of the wines is greatly improved by adding a certain quantity of glucose to the fermenting-vat.

Sparkling wines, such as champagne, are prepared from a black grape, the juice of which generally contains more sugar than the white grape; but in order to avoid colouring the juice, great care is taken not to rupture the husk of the grape or of the stalks. The grapes, gathered in warm weather, are carried with great care to the press, when, by a first and gentle pressure, the juice which is to make wine of first quality is obtained, while the must, being again stamped, and more powerfully expressed, furnishes a juice from which pink champagne is made. A third and fourth pressing is sometimes made, but the products are added to the ordinary red wines. The white or pink juice is allowed to ferment in large hogsheads, where it is freed from the greater portion of its yeast, which floats on the surface with the scum. In 24 hours the juice is drawn off into other hogsheads, which are kept nearly filled, and

imperfectly closed, so as to allow the disengagement of carbonic acid. In a month it is drawn off and fined for the first time, a second fining being applied after the following month, after having drawn it off, and a third one in the month of April, when it is bottled. Three to five per cent. of its weight of sugar-candy, dissolved in an equal weight of water, is then added to the wine. The bottles are very carefully closed with corks, held down by iron wire, and surmounted by a metallic cap; and they are laid upon their side, a lath of wood being placed between each two bottles. A portion of the sugar added undergoes alcoholic fermentation, under the influence of the yeast which still exists in the wine, but the carbonic acid, finding no escape, remains in solution in the liquor, which also retains a sweet taste, produced by the portion of the sugar which has not fermented.

## MANUFACTURE OF BEET-SUGAR.

§ 1727. The sugar-beet cultivated in France for the production of beet-sugar, is the species called the *white Siberian sugar-beet*, and shows the following average composition :

Water .....	83.5
Sugar .....	10.5
Cellulose.....	0.8
Albuminous substances .....	1.5
Various organic substances, and mineral salts	3.7
	<hr/>
	100.0

The beets are taken out of the ground when they have acquired their full growth, and carefully separated from those which have been injured by the operation, since the latter do not keep, and should be used immediately. The beets are made into heaps in the field, and covered with leaves, until there is danger of frost, when they must be housed, or buried in pits. The upper part of the root, at the starting-point of the stalk, is cut off, because this portion is harder and contains but little sugar.

The beets, after being cleansed and washed, are thrown into a machine which reduces them to as fine a pulp as possible and breaks up the cells. The pulp is placed in woollen bags, laid on each other, and between which metallic plates are introduced; after which the mass is compressed by a screw-press, and the juice which flows out, and which constitutes about 0.4 of the juice contained, collected. The bags and plates are then placed under the platform of an hydraulic press, which is unscrewed after having maintained the pressure for about 10 minutes, when the bags are placed two by two between two plates, and again still more powerfully compressed. In this manner, 75 to 80 per cent. of beet-root juice may be extracted, only about 15 parts being left in the pulp.



§ 1728. As the juice soon changes, it is essential to raise it, as quickly as possible, to a high temperature, in order to destroy the ferments; and to saturate with lime the free acids, which would soon convert a portion of the sugar into sugar turning to the left. For this purpose, the juice, on leaving the press, is conveyed into a double-bottomed boiler, heated by steam, and the temperature is rapidly raised to  $140^{\circ}$  or  $158^{\circ}$ , after which it is conveyed into another boiler, also heated by steam, where the *defecation*, or treatment with lime, is effected. Hydrated lime is usually made by pouring on quicklime 10 times its weight of boiling water, and, when the lime is entirely slacked, passing it over a metallic sieve, which arrests the grains of sand and the non-decarbonated portions. The juice is first heated to  $167^{\circ}$  in the defecating boiler, the milk of lime is then added, and the whole is stirred, to render the mixture homogeneous; when the temperature is raised to  $212^{\circ}$ , the supply of steam being cut off when ebullition commences. The lime combines with the free acids, the albuminous substances, the fatty and colouring matters, and produces insoluble compounds, effecting at the same time a kind of clarification, by carrying down, with the insoluble compounds, organic remains which were suspended in the juice. A thick scum having formed on the surface of the liquid, the latter is kept from boiling, in order to prevent its rupture by the bubbles of steam. The proportion of lime added varies with the nature of the beets and with their freshness; only 3 lbs. for 1000 pints of juice being used in the beginning of the season and with fresh beets, which quantity is gradually increased, and frequently reaches 10 lbs., before the close of the season. An excess of lime remains in the liquor, and forms a deliquescent compound with a portion of the sugar, which must be lessened as much as possible, because it causes a loss of sugar. In some factories, it has been endeavoured to saturate it with a proper quantity of acid.

§ 1729. When the defecation is terminated, the liquor is drawn off and filtered through animal charcoal, the filters used for this purpose being large sheet-iron cylinders, having a false bottom, pierced with holes, like a cullender. A cloth is extended over the bottom, on which is spread very coarsely powdered animal charcoal, added in successive layers, until it fills the cylinders to  $1\frac{1}{2}$  foot from the top, when another cloth is laid upon it, and is covered by another metallic plate pierced with holes; each filter receiving 6000 to 8000 lbs. of charcoal. The filters should be kept constantly filled with fluid, which is easily done by means of a stopcock. After this process, by which the juice loses a portion of its colouring matter, and the lime in excess, which adhere to the charcoal, it is conveyed as rapidly as possible into the concentrating boilers, which are generally shallow, and are heated by the circulation of high-pressure steam through copper tubes arranged over their bottoms. The juice is raised to a temperature of  $70^{\circ}$  in 10 or 12 minutes. The workman judges,

by signs learned by experience alone, if it is properly concentrated, or if the *boiling* is completed. During the ebullition, which terminates at a temperature of  $266^{\circ}$  to  $275^{\circ}$ , a considerable portion of the sugar is altered, and, to diminish the loss, the evaporation must be effected as rapidly as possible. This operation has been greatly improved by boiling in vacuo, that is in close boilers, heated by steam, and brought into communication with worms and receivers in which a vacuum is made; when ebullition takes place at a lower temperature, the quantity of sugar changed is much smaller.

§ 1730. When the syrup is properly boiled, it is collected in a cooler, which usually receives the products of 5 or 6 boilings; and its temperature then falls to about  $176^{\circ}$ . Crystallization then commences, but as soon as any crystals form, they are detached from the sides, and the syrup stirred to bring them again into suspension. When the temperature has fallen to  $130^{\circ}$  or  $122^{\circ}$ , the syrup is poured into large conical moulds of metal or baked clay, resting on the point, which is furnished with a hole previously stopped with a plug of wet muslin. The moulds are ranged on long benches, with openings through which the escaping fluids fall into zinc gutters, whence they flow into reservoirs. The temperature of the room containing the moulds should be about  $86^{\circ}$ . Crystallization is completed in 24 or 36 hours, when the plug is removed from the opening in the mould, and the point of the loaf pierced with an awl, so as to draw off the molasses, which is again concentrated, even further than the original syrup, and crystallized in moulds. When the molasses is too highly coloured, as happens sometimes, it is diluted with a sufficient quantity of water, filtered through animal charcoal, concentrated and recrystallized. The syrup which drains from the second sugar is frequently subjected to the same process for a third time, but the crystallization then requires a great length of time.

When the sugar has drained sufficiently, the loaves are *loosened*, that is, the moulds are inverted, and the loaves detached by gentle blows; after which they are placed in the wareroom, protected from dampness. This is raw beet-sugar, which requires refining before being fitted for consumption.

## MANUFACTURE OF CANE-SUGAR.

§ 1731. Of all sacchariferous plants, sugar-cane is the most rich in sugar, since it yields 0.90 of juice, containing from 0.17 to 0.22 of crystallizable sugar; but in the majority of the colonies its manufacture is still so rude that nearly one-half of the sugar contained in the cane is lost. The richest variety of sugar-cane is the *ribbon-cane*, or *Otaheite cane*, containing, on an average,

Water.....	72.1
Sugar.....	18.0
Woody tissue.....	9.9
	<hr/>
	100.0

It leaves about 0.4 of ash containing a considerable quantity of silix, like that of all the gramineæ; and the ash consists of

Silix.....	68
Potassa.....	22
Lime.....	10
	<hr/> 100

§ 1732. When the canes are cut, they soon become damaged by fermentation, and should therefore be carried immediately to the mill. The latter is composed of large stone or cast-iron cylinders, between which the canes are crushed; the best being provided with five crushing-cylinders, so that the cane is compressed four times. They are turned by a water-wheel or by steam; and in the majority of sugar-works only about 50 kilog. of juice are extracted from 100 kilog. of cane, while in the best mills about 65 are obtained; 40 kilog. of juice being in the former case left in the *cane-trash*, and 25 in the latter. The woody fibre of the cane renders it very difficult to extract the juice completely, which would require greater power; and in the colonies the trash is, generally speaking, the only fuel used. The rapid and perfect extraction of the juice is the most important part of the process, and that which produces the greatest loss of sugar when not well performed. The fresh cane-juice, which, in addition to the sugar, contains merely very small quantities of albuminous substances, is allowed to remain for an hour in a reservoir to become clear, and is thence conveyed into the boilers, five of which generally make a set. The first, which is the most remote from the furnace, is used for defecation, (or tempering;) in which case only  $\frac{1}{10}$  of the quantity of lime necessary for the defecation of beet-sugar is used; about 0.2 or 0.3 for 1000 of juice. It is then heated to boiling, and rapidly skimmed. The defecated juice is thence conveyed into the second boiler, where evaporation commences; the skimmings from this boiler being removed and thrown back into the first. The liquor then passes into the third boiler, where the evaporation is continued; and during its sojourn in this boiler, the workman ascertains if it has been properly defecated, or if it requires the addition of a small quantity of lime. He then transfers the liquid into the fourth boiler, where it is concentrated to the consistence of syrup; and lastly into the fifth, where it is concentrated to the consistence suitable for crystallization.

In the best establishments the boilers rest on pivots in their central line, and are placed below each other, which arrangement greatly facilitates and accelerates the working.

The boiling is then run off into large flat reservoirs, where it is allowed to cool and crystallize for 24 hours, when the granular mass is poured into moulds, in which the crystallization is completed, and is finally drained.

The operation generally yields in most of the works,

Brown sugar.....	55 to	65
Sugar which remains in the molasses, for the greater part uncrystallizable.....	25 to	20
Sugar left in the trash.....	80 to	75
	<u>160 to</u>	<u>160</u>

In several important sugar-works, an apparatus for evaporating in vacuo has been tried, which considerably diminishes the loss of sugar in the molasses, and also furnishes a better article; but the primitive cost of such apparatus, combined with the want of fuel, will for some time prevent this more perfect process from being generally introduced.

Molasses is used in the manufacture of several alcoholic liquors, such as rum, ratafia, etc.

## SUGAR-REFINING.

§ 1733. A large quantity of cane-sugar is consumed in the state of brown sugar, while the greater portion of it is refined; and raw beet-sugar must also be refined, as otherwise the flavour and smell of the beets would render it unfit for use. The refiner generally mixes cane and beet-sugar in proportions which facilitate the process. Cane-sugar, during its voyage from the colonies, has generally undergone some change, and contains a small quantity of acid, while beet-sugar, on the contrary, contains a small quantity of saccharate of lime; and by mixing them in proper proportions, the acid of the cane-sugar is saturated by the lime of the beet-sugar.

The raw sugars being mixed on a table made of flag-stones, and passed through a sieve, the mixture is dissolved in 30 per cent. of its weight of water. The solution is effected in boilers heated by steam, and placed sufficiently high to allow the syrup to fall directly into charcoal filters, after which the *clarifying* is commenced. This operation consists in adding to the syrup 5 per cent. of its weight of finely powdered animal charcoal, (bone-black,) and 1 or 2 of an albuminous substance coagulable by heat; bullock's blood, defibrinated by beating, and diluted with 4 times its weight of water, being generally used. The liquid is stirred, and allowed to boil, when the syrup is run into peculiarly shaped filters, which arrest the substances in suspension and the scum. The best filters are those made of an upright wooden case, containing a great number of bags, made of cotton or woollen drugget, the mouth of which is above the top of the case, while the lower part passes through the bottom and opens below. The muddy liquor being poured into the case, filters from without into the bags, which are kept from collapsing by hoops of wood or iron, by which means filtration ensues over a large porous surface, and the filters are moreover easily washed. The residue in the case is washed with fresh water, which

furnishes a weak solution of sugar, used to dissolve the new sugars; and is then sold as manure, under the name of *refinery-black*.

The clarified syrup is immediately filtered through charcoal, in an apparatus resembling that used for the bleaching of tempered sugar-beet juice, (§ 1729,) and is then conveyed into the boilers. In almost all the large refineries, it is now boiled in an apparatus calculated to evaporate in vacuo. The concentrated syrup is collected in kettles in which the temperature is raised to  $176^{\circ}$ , in order to retard crystallization, and redissolve the crystals which had begun to form in the evaporating kettles, where the boiling point is not very high. Crystallization soon commences in this kettle, while the temperature falls, and the liquid is frequently stirred, and the mixture of syrup and crystals poured into moulds, which are placed in a room contiguous to the boilers. The moulds are generally of baked clay, and are 50 centimetres in height, and from 15 to 22 wide at the base. Before using new moulds, they are kept filled for several days with a thin pap of clay, which closes the pores of the earthenware, and prevents the absorption of the syrup and the adhesion of the loaves. The moulds are perforated at the lower part, the holes being closed with a plug of wet muslin; and the moulds are arranged on a double bench, furnished with openings, and of which the lower part, made of zinc, conveys the drippings into a canal communicating with a reservoir kept for the purpose. When the moulds are filled to about 1 centimetre below the top, they are allowed to rest for some time; when there forms on the surface of the syrup a crystalline crust, which is broken, and the broken crystals are thrown to the bottom, the syrup being stirred at the same time in order to equalise the temperature, which always falls most rapidly toward the apex of the cone. The crystallizing-room is kept at a temperature of about  $95^{\circ}$ . After remaining 8 or 12 hours in this room, the moulds are carried into low apartments with brick floors, and heated by steam conveyed in pipes on the floor or around the walls. The plug is then removed from the hole in the moulds, and the loaf pierced with an awl; when it is allowed to drain, and in 12 hours the base of the loaf is nearly white and dry.

The sugar, which now is called *drained green* or *raw sugar*, is then left in the moulds for 6 or 7 days to complete the draining, after which the workman smooths the base of the loaf with a plane, and adds to it a layer of purely white sugar, for which he generally uses scrapings of refined sugar, in order to make the base of the loaf perfectly level, as it would otherwise be disfigured by a depression in the centre. The *claying* is then commenced, which consists in pouring into each mould a paste of clay diluted with water to the thickness of 2 or 3 centimetres. The water from the clay, filtering slowly through the loaf, becomes saturated with nearly pure sugar in the upper strata, which are nearly bleached by draining, and displaces in the lower parts the coloured molasses which moisten the

porous crystalline mass. After 7 or 8 days of claying, the clay forms a firm coating on the surface of the loaf, which is removed by a spatula. The base of the loaf is again smoothed, and it is subjected to another claying resembling the first. These two processes generally produce refined sugar, although a third claying is sometimes necessary.

After the last claying, the loaves are laid on their sides, and the bases being again smoothed, the moulds are slightly tapped, in order to detach the loaves from their surfaces, and thus allow the last portions of syrup to pass through more easily. The moulds are then placed in their former position, to collect the syrup in the apex and cause it to flow out as completely as possible; after which they are set on their bases, and thus left for 24 hours, in order to spread the syrup yet contained in the apex, which would sensibly colour the latter, throughout the whole loaf. These alternate positions are repeated several times, until the whole mass has acquired a uniform colour; after which the loaves extracted from the moulds are exposed to the air for 24 hours, and then dried in ovens at a temperature not exceeding  $113^{\circ}$ .

In some manufactories, *decolouring* is substituted for claying. This operation consists in pouring upon each loaf, in the mould, a certain quantity of a syrup saturated with sugar, and purer than that which moistens the loaf, when the latter syrup is displaced by the syrup added, and escapes through the apex of the mould. The first "*clairce*" is replaced by a second, composed of a syrup still purer than the first, and so on, until the last *clairce* consists of perfectly refined sugar. This process is much more expeditious than that of claying.

The name of *lumps*, or *bastards*, is given to sugars of inferior quality, for the making of which the coarsest raw sugar, the green syrups, and residues are used. They are clarified and boiled as are sugars of superior quality, but are crystallized in larger moulds, and the loaves are *decoloured* or *clayed* once oftener than sugars of first quality. The apex of the loaf is generally coloured, and must be removed.

A kind of white loaf-sugar, called *dried sugar*, has been for a long time manufactured at Marseilles, (*sucré tapé*.) It is prepared by rasping the best quality of lumps without allowing them to dry, passing the substance through a coarse sieve, and introducing it into small moulds, previously moistened, into which it is pressed with a flat pestle. After some time the loaves are taken out and placed in a stove.

## BONE-BLACK.

§ 1734. Animal charcoal, or bone-black, used for bleaching sugar, is generally made in the vicinity of large cities, because bones are there cheaper and more easily procured. The bones form about  $\frac{1}{3}$

of the weight of the recently slaughtered animal; and those which are of sufficient size and thickness are set apart for the use of turners.

The fat, used in the manufacture of stearin candles, is first extracted from the bones intended for making bone-black, by breaking them into pieces and heating them with water in large boilers, in which they are frequently stirred, when the fat separates and floats on the surface. The bones are removed from time to time with a strainer, and fresh ones added. A portion of the bones, before being carbonized, is used for the preparation of gelatin, (§ 1662.)

The bones, after being deprived of their fat, are drained and dried in the air, and then carbonized in cylinders, or in large cast-iron or earthen pots, generally about 1 foot in diameter, and  $1\frac{1}{2}$  foot in height, which are piled on each other or ranged in rows in large furnaces heated to redness with bituminous coal, which temperature having been kept up for 6 or 8 hours, the pots are removed. When they are perfectly cold the bone-black is removed and ground between cylinders; all dust being avoided as much as possible, because enough is always formed for the clarifying of sugar, (§ 1733.) The dust and variously sized grains are separated by bolting and sifting in sieves with meshes of suitable size.

Bone-black which no longer exerts any bleaching power on juices and syrups, may have this power restored, and be made useful in future operations, by removing the soluble substances in them by washing, and recalcining them, which carbonizes the adhering organic matters and exposes the carbonized portions. Their surface, however, being still covered with a pellicle of vegetable charcoal, which diminishes sensibly their activity; the former is removed by rubbing them slightly between horizontal grindstones which do not exert sufficient pressure to crush them, and by separating the dust formed by bolting. By this reviving, bone-black loses 4 to 5 per cent. of its weight; but the operation may be repeated 20 or 25 times on the same charcoal.

#### MANUFACTURE OF SOAPS.

§ 1735. We have mentioned (§ 1594) that the salts formed by fatty acids with the metallic oxides are called *soaps*. Soaps of which the base is potassa, soda, or ammonia, are the only ones soluble in water; and soaps of potassa and soda alone are used for washing and for the toilet. In commerce, soaps are divided into *hard soap*, of which the base is soda, and *soft soap*, of which the base is potassa; the latter being more generally used in northern countries, while in France the hard soap is preferred. Soaps formed by the same base are harder in proportion to the melting point of the fatty substances used in saponification.

Soaps are made by boiling fatty substances with more or less concentrated lyes of caustic potassa or soda; which are obtained by decomposing the alkaline carbonates, when cold, by hydrated lime.

False-bottomed vats are generally used, and on the upper bottom, which is covered with straw, the slaked lime is placed, mixed with the powdered alkaline carbonate, and it is then covered with water to the depth of about 5 inches. In a few hours the liquid has filtered through the solid matters, and collected on the lower bottom, whence it is then drawn off into a separate vat, to be pumped back into the first vat, and once more to filter through the lime; this process being continued until the alkali is completely deprived of its carbonic acid. By washing the remaining lime with water, alkaline lyes are obtained, which are generally used in the first stage of saponification of fatty substances. Saponification is effected in large boilers, which are first filled to one-fourth with weak lye, and into which the fatty substance is gradually poured, taking care to constantly stir the mixture; weak lye and fat being then added successively until the boiler is sufficiently filled. An emulsion of soap, with an excess of fat, is first formed in a liquor which contains but little free alkali, and which must be kept uniform by continual stirring, when a stronger lye is introduced, which converts the soap having an excess of fatty acids into a more basic and soluble soap. This more highly charged lye is added by different portions at a time, and, in the last place, it is mixed with common salt, or other alkaline salts, which entirely precipitate the soap and separate it from the lye. It is allowed to cool, and the aqueous liquid containing the glycerin, the alkaline salts which have effected the separation of the soap, and the excess of alkali, is drawn off. A last concentrated lye being then added, the whole is heated to ebullition, which temperature is maintained until the lye has attained a density of 1.15 to 1.20, when the supernatant soap is removed and run into moulds, and, after it has become sufficiently solid, is divided in parallelopipedons of proper dimensions by means of a wire.

§ 1736. Marseilles soap is that most esteemed, and is made from caustic soda and inferior quality olive-oil yielded by the hot expression of the olive-must from which first quality olive-oil has been already obtained. Two kinds of artificial soda are used for these soaps, one called *sweet soda*, which should be as pure as possible, since it affects the saponification, and the other highly charged with sea-salt, and called *salt soda*, which is used for furnishing to the first soap, having an excess of fatty acid, the quantity of base necessary to entirely precipitate it from the liquid.

The sweet soda, broken up, is mixed with  $\frac{1}{8}$  of its weight of caustic lime, previously slaked and placed in vats of mason-work, called *barquieux*, where the mixture is lixiviated several times, furnishing liquids of decreasing strength. Saponification is effected in large kettles with sloping sides, made of bricks, and with a copper bottom: a lye marking  $12^{\circ}$  Baumé being first introduced and boiled, the oil is gradually added, and the whole is constantly stirred. After some time a lye marking  $15^{\circ}$ , and at a later period a lye marking  $20^{\circ}$ ,



is introduced. The whole operation, called *empâtage*, lasts about 24 hours, and produces a soap with an excess of fatty acid; it being important that the soda should be as free as possible from sea-salt. Having reached this point, the *relargage* is commenced, the object of which is to make the soap more alkaline and separate it from the lyes; to which effect a workman throws in gradually, on the surface of the kettle, a salt lye, marking from  $20^{\circ}$  to  $25^{\circ}$ , while another stirs the whole continually, when the paste, hitherto homogeneous and viscid, is converted into clots, which separate from the aqueous liquid. It is allowed to rest for 2 or 3 hours, when the lye is drawn off. After this operation, which is called *épinage*, it is again treated twice with fresh salt-lye, in order to give the proper consistency to the soap; and then, after having drawn off the last water, the paste is worked with shovels to render it homogeneous, small quantities of weak lyes or fresh water being frequently added, according to the nature of the soap to be made; after which it is run into moulds, and cut into small pieces after cooling.

§ 1737. Two kinds of soap are found in commerce; the *white* and *marbled soap*. The bluish veins observed in the latter are produced by a small quantity of soap having a base of alumina and protoxide of iron, and by sulphide of iron yielded by a small quantity of sulphide of sodium which always exists in the lye. Of themselves, these foreign substances are of no use, and may even in some cases be injurious; but as their presence is a certain index that the soap does not contain more than 30 per cent. of water, marbled soap is highly valued on that account. When the paste contains more water, it is more fluid and light, and metallic compounds are easily deposited in it, and cannot be distributed through the soap in veins.

White soap is made by diluting the paste at a moderate temperature, in weak lyes, and allowing it to rest in tight kettles; when the soaps of alumina and iron falling to the bottom, the supernatant white soap is removed and carried to the moulds. In order to prepare marbled soap, less lye is added, and the soaps of alumina and iron are not so completely deposited, and separate in veins throughout the mass. Cakes of marbled soap generally lose their colour in the air, because the protoxide and sulphide of iron are converted into sesquioxide; but the marbling is always seen in freshly cut soap. Marbled soaps generally contain 30 per cent. of water, and white soaps not less than 40 or 50.

Resins form, with the alkalies, salts which exhibit characters resembling those of the soaps; and yellow soaps are now made, the fatty acids of which are partly replaced by colophony.

§ 1738. Soft soaps are made with hempseed, linseed, colza, and other oils, the base being potassa. Their natural colour is of a brownish-yellow, while a greenish tinge is generally given to them by the addition of a small quantity of indigo. The process is nearly

the same as that of making hard soaps, except that lyes of potassa are substituted for those of soda; and when saponification is completed, and the soap has become transparent, it is evaporated to the proper consistency, and run into hogsheads. This soap is always more alkaline than soda-soap, and dissolves more easily in water.

Toilet-soaps are made with soda, and are generally highly hydrated, being prepared either from olive-oil or tallow, and their agreeable odour is owing to essential oils mixed with them in the moulds. Colourless or coloured transparent soaps are made by dissolving in alcohol well-dried soap made of beef-suet, concentrating it properly by distillation, and pouring the limpid and transparent fluid into moulds, where it becomes solid. Various organic colouring matters may be incorporated with it.

#### CHEMICAL PRINCIPLES OF THE ART OF DYEING.

§ 1739. The art of dyeing has been of late so scientifically cultivated, that it would require much greater space than the limits of an elementary course can afford, to give a complete idea of it; and we shall therefore be obliged to confine ourselves to the explanation of the chemical principles on which is based the preliminary preparation of the textile fibres to render them fitted for the manufacture of tissues, and those on which is founded the art of fastening colouring matters.

##### *Preliminary Preparation of the Textile Fibres.*

§ 1740. The textile fibres used in manufactures are either of vegetable or animal origin; the first being chiefly hemp, flax, and cotton, and the second wool, hair of animals, and silk spun by the silkworm.

Cotton is nearly pure lignin, while hemp and flax are composed of lignin in long filaments, which, when dry, adhere to each other by means of a gelatinous substance, called *pectin*, although it differs probably from that found in fruits, and which must be removed to render them fit for spinning and weaving. For this purpose, they are *rotted*, which operation consists in plunging them, tied in bundles, into water, where they are left until fermentation commences, which is manifested, in stagnant waters, by a very disagreeable odour. The bundles are then withdrawn from the *rotting-pond*, and, after having been dried in the air, are subjected to mechanical operations, of which the object is to detach the foreign substances, which have become friable by the desiccation ensuing on the rotting, and to isolate the fibres. Hemp and flax thus prepared are fit to be converted by spinning into *unbleached thread*, which may be immediately used for weaving. Cotton undergoes no preliminary preparation, and may be immediately spun and woven.

§ 1741. Wool, as it is found on the living animal, is impregnated

VOL. II.—3 Q

with a considerable quantity of foreign substances, commonly called *grease*,\* (suint,) and which consist essentially of substances soluble in water, and fatty substances insoluble in that fluid. Sheep are usually washed before being shorn, and then yield what is called *washed wool*, which has thus lost a large portion of its soluble matters, and a portion of the fatty matters, which separated in the state of an emulsion. Wool which has not undergone this operation is called *unwashed wool*; and the process by which the grease is removed from wool is known by the name of *scouring*.

Unwashed is scoured with washed wool, in a bath of 300 litres of water and 72 to 78 of putrid urine, the whole being heated to 122° or 140° for *soft wool*, and to 158° or 167° for *harsh wool*. After dipping 3 or 4 kilog. of unwashed wool into the bath, and stirring it with a stick for 10 minutes, they are removed, and allowed to drain over the kettle; the same being done with another lot of 3 or 4 kilog., until about 40 kilog. in all have been thus treated. 6 or 7 kilog. of putrid urine are then added, and 50 kilog. of washed wool passed through it, which is scoured, both by the carbonate of ammonia of the putrefied urine and the alkaline substances yielded by the unwashed wool. The same operation is repeated on a new lot of 40 kilog. of washed wool; after which a new dose of 6 or 7 litres of putrid urine is added, and 20 kilog. of unwashed wool washed in it. This alternate scouring of washed and unwashed wool is continued during the whole day, adding urine at each fresh quantity of unwashed wool. After this operation, the unwashed should be considered as washed wool, and treated accordingly.

When the wool-scourer has no unwashed wool, he makes his bath of 650 litres of water and 300 litres of urine, heats it to 120° or 140°, and passes through it 30 kilog. of wool in 5 lots, each of which he leaves in the bath for 12 or 15 minutes, after which he adds 1 litre of water and 2 of urine, and then scours an additional portion of 30 kilog., and so on. Some scourers add marly clay to their bath.

Washed wool contains less than 15 per cent. of grease, while unwashed contains much more; and, by washing, scouring, and drying, loses as much as 60 or 70 per cent. of its weight. When the washed wools contain less than 5 per cent. of grease, they are scoured with soap or carbonate of soda.

The nature of the fatty matters of the grease is peculiar, and they have been called *stearerin* and *elaierin*; the first of which is souble but uncrystallizable, while the second is oleaginous. These fats are not saponified by weak alkaline lyes, but, when they are boiled for a long time with a solution of caustic potassa, the liquid is found to contain two salts of potassa, formed by peculiar fat acids, which have been called *steareric* and *elaieric acids*; while nothing analo-

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\* In England it is called the *yolk*.—TRANS.

gous to glycerin has yet been found. The oxygen of the air may possibly have some share in the formation of these fat acids.

After scouring, the wool is washed in river-water in willow baskets. When it is intended to be perfectly white, it is exposed for some time in a moist state in rooms in which sulphur is burned, when the sulphurous acid finishes the bleaching, (§ 131,) and the excess of it is removed by fresh washings. It is important not to prolong too much the action of the sulphurous acid, because it exerts a decomposing agency on the nitrogenous substance of the wool.

Wool contains, in addition, a proximate sulphuretted principle, which may be separated by successive immersions in limewater. Wool which has been heated with a weak alkaline solution disengages sulphhydric acid when it is again heated with acidulated water, and is blackened when boiled with a solution of a salt of lead or protoxide of tin.

§ 1742. Raw silk, as it is obtained from the cocoons, is impregnated with a gelatinous substance, which makes it very stiff, and generally gives it a golden-yellow tinge. This substance, which forms about  $\frac{1}{4}$  of the weight of raw silk, dissolves readily in alkaline liquids; but as the caustic alkalies attack the silk itself, soap is almost always used, and sometimes, though rarely, carbonate of soda.

This operation, which is called *scouring* (*décreusage*) *the silk*, is divided into three stages: the *ungumming*, (*dégommage*), *boiling*, and *bleaching*. The ungumming is done in a tinned boiler, containing, for every 100 parts of silk, 1800 or 2500 parts of water and 30 of soap. It is first boiled to dissolve the soap, and then cold water is added, so as to lower the temperature to about  $200^{\circ}$ , when the silk is dipped into it in skeins, supported by sticks, called *lisoirs*, being there left until all the gelatinous matter is dissolved, and afterward wound on a bobbin. This operation lasts from  $\frac{3}{4}$  to  $1\frac{1}{2}$  hour. Several skeins are then united, forming a *hank*, which is boiled for  $1\frac{1}{2}$  hours in a bath containing 20 or 30 parts of soap for 2000 of water, which constitutes the *boiling*, (*cuite*.) The hanks are undone, twisted into skeins, wound on a bobbin, and then washed in a weak solution of carbonate of soda and in river-water. The bleaching consists in dipping the silk held by the lisoirs into a bath heated to  $203^{\circ}$ , and composed of 300 litres of water and from 500 to 750 grammes of white Marseilles soap. Silks which are intended to be brilliantly white are exposed, in addition, to sulphurous acid.

#### PRELIMINARY PREPARATION OF STUFFS.

§ 1743. Before being printed, cotton stuffs are *singed* or *shorn*, with the intention of removing the filaments which project from the tissue. The shearing is performed by machines, called *shearing-machines*, composed of two revolving cylinders, one of which, furnished with brushes, raises the nap, while the other, provided with knives arranged spirally, shears it. In singing, the stuff is passed

rapidly over a metallic cylinder, heated to nearly a white-heat, which burns off the down.

§ 1744. Cotton stuffs which are intended to be perfectly white are previously *bleached*, which operation is also more or less completely performed on goods which are to be printed.

Linen and cotton goods are bleached by two different processes:

1. By washing them in alkaline lyes, and exposing them on the grass;
2. By chlorine or the alkaline hypochlorites.

The first is the oldest, and was used particularly for bleaching flax and hempen goods. It is divided into the following operations:—1. *Scouring*, which consists in dipping the stuffs for 24 hours in a weak solution of caustic potassa, heated to about  $99^{\circ}$ , washing, and then boiling them for 20 minutes in the same alkaline lye. 2. The *boiling*, which consists in boiling (as was stated § 1743) the scoured stuffs, after having washed them in water, and compressed them between cylinders. 3. *Bleaching*, which consists in boiling them for 6 hours with an alkaline lye, containing 1 part of caustic potassa for 16 parts of stuff, washing them, and exposing them for 5 or 6 hours on the grass; the alkaline washings and exposure on the grass being renewed until the stuffs are perfectly bleached. During the exposure on the grass, the colouring matters are bleached by the influence of the solar rays and moisture; the absorption of oxygen converting them into new substances more readily soluble in the alkaline liquors. Lastly, the stuffs are passed through water heated to  $105^{\circ}$  or  $120^{\circ}$ , containing about  $\frac{1}{60}$  of sulphuric acid, which dissolves the metallic oxides; after which they are washed and calendered.

This process requires a great length of time, and bleaching by chlorine or the hypochlorites is more expeditious. The chlorine acting on the colouring matters, in the presence of water, decomposes the water into hydrogen, which combines with the chlorine to form chlorohydric acid; while the oxygen in the nascent state oxidizes the resinous and colouring matters, and renders them soluble in alkaline lixivæ. The hypochlorites are reduced to the state of metallic chlorides, and act at the same time by means of the nascent oxygen given off by the hypochlorous acid and the base; while the concurrence of an acid effecting the decomposition of the hypochlorites hasten the bleaching. Thus in both processes it is in the end always an oxidizing action which effects the bleaching and destruction of the foreign substances.

Hypochlorite of lime, dissolved in water, is now solely used in bleaching; and it is preferable to all dilute solutions, because it is less liable to injure the ligneous fibre of the tissue; although the bleaching then requires more time.

The stuffs, after being passed over the heated cylinder to be singed, are immediately dipped into a vat filled with water to cool them, where they then remain for 24 hours, and lose a considerable

portion of their soluble principles. They are then to be perfectly dried, either by being beaten or compressed between cylinders, and then kept for 12 hours in a vat filled with water heated by steam, where they are arranged in alternate layers with slaked lime. After being again beaten, they are left for 12 hours in a lye of caustic soda, consisting, for 300 parts of stuffs, of 10 parts of caustic soda for 1500 of water. This lye is replaced by another containing only 7.5 of soda, which is also allowed to act for 12 hours; after which the stuffs, pressed dry, are passed through the hypochlorite of lime, and then through sulphuric acid. The bath of hypochlorite generally contains 0.15 litre of chlorine in a litre of water; and the stuffs, after being immersed in it, are passed between two wooden cylinders, descending thence immediately into a bath acidulated with sulphuric or chlorohydric acid, which hastens the bleaching by isolating the hypochlorous acid. After being washed in fresh water, they are for a second time subjected to the action of alkaline lyes, hypochlorite of lime, and the acid bath; and lastly, after another washing in fresh water, they are dried in drying-machines, and more *body* is given to them by dressing them with starch.

#### *Mordants.*

§ 1745. The tissues of muslin or linen stuffs have, for a great number of colouring substances, an affinity sufficiently powerful to fasten them on their surface, and to acquire a deep colour; while the combination is rarely strong enough to enable them to resist washing, particularly with alkaline soaps. They are made fast, and at the same time the colour is heightened, by previously depositing on the tissues certain substances which have a greater affinity for these tissues than the colouring matters, and which possess, at the same time, the property of forming with the colouring matters compounds sufficiently fixed to resist washing in fresh water and in soap-suds. These substances, which thus play an intermediate part between the woven fabric and the colouring matters, are called *mordants*. The affinities by virtue of which they are fastened on the fabric exhibit this essential difference from those observed in ordinary chemical operations, that, in the latter, combination generally ensues only between disaggregated substances, and if one of the substances is originally aggregated, it becomes disaggregated by the simple fact of combination; while, in dyeing, the woven fabric retains its form and consistence without being in the slightest degree disaggregated by the mordants and colouring matters.

Certain mordants do not change the shade of the colouring matters, such, for example, as the salts of alumina and chlorides of tin; while others, on the contrary, alter the colour, as the salts of iron, manganese, and copper. The salts of alumina used as mordants are the sulphate, and acetate of alumina, and alum; the fastening of colours with alum being also called *aluming*.

In order to alum cotton, flax, or hempen stuffs, they are left for 24 hours in a tepid bath containing 1 part of alum for 6 parts of fabric, when a portion of the alum adhering to the stuff renders the latter fit for dyeing. For dark colours, the ordinary alum of commerce is used; Roman, or purified alum, (§ 600,) being preferred for bright colours, because common alum always contains a small quantity of sulphate of iron, which would modify the shade.

Wool is alumed by being first boiled in bran-water for an hour and washed in fresh water, and then kept for 2 hours in a boiling solution which contains 10 to 15 per cent. of alum, a small quantity of cream of tartar being generally added, which facilitates the deposit of the alumina on the tissue, perhaps by converting a portion of the sulphate of alumina into a tartrate of more easy decomposition. When the wool is alumed, it is left to rest for 2 days, before dyeing, in order to render the combination of the mordant with the fibres more intimate.

Silk is alumed when cold, by keeping it for 15 or 16 hours in a bath containing  $\frac{1}{50}$  of alum; after which it is removed and washed.

Acetate of alumina, which is often used as a mordant for ligneous stuffs, and for certain colours, is prepared by decomposing alum by acetate of lead; the solution of acetate of alumina thus obtained being generally thickened with starch or gum.

Stuffs of lignin mordanted with alum, are again subjected, before being dyed, to another operation, the effect of which is not well understood: they are immersed, for some time, in two baths of water, containing 6 or 8 per cent. of cow-dung. To the first of these baths a certain quantity of chalk is added, the intention of which appears to be to saturate the acid partly adhering to the tissue with the mordant; while the second contains only water and dung. The temperature of these two baths varies according to the nature of the stuffs and that of the mordants. The cow-dung appears to act by means of the phosphates it contains, for a mixture of phosphate of soda and lime can be substituted for it.

Protochloride of tin is chiefly used for obtaining the oxide of tin as a mordant, which adheres very firmly to the tissues. Bichloride of tin is often used for freshening colours, particularly those of cochineal and madder. The mordant of oxide of iron is furnished by the protacetate of iron, prepared by the reaction of pyroligneous acid on old iron.

### *Dyeing.*

§ 1746. After the stuffs are mordanted, they are immersed, in order to be dyed, in solutions of colouring matter, of various temperatures, and then left for a longer or shorter time, according to the nature of the stuff and the tint of colour to be obtained. It is essential that all parts of the fabric should remain the same length of time in the dye; to which effect it is rolled around a wooden roller suspended

over the dye-tub, and is unrolled through the tub; this process being continued until the colour has obtained the shade required. In order to obtain a uniform shade, it is better to use several successive baths of different strength, commencing with the weakest. The baths are sometimes composed of a single colouring matter, and sometimes of a mixture of several, while at other times the stuff is passed successively through two baths containing different colours, and thus an intermediate shade is obtained. The colours are fastened by washing in soapsuds or in other solutions.

It would lead us too far to give a description of the methods of preparing the different solutions for dyeing, and the manipulations of the process.

*Calico and other printing.*

§ 1747. Designs of various colours are printed on smooth goods; the impression being effected either by an actual printing off of the colouring matter by means of wooden blocks carved in relief, or engraved rollers of copper; or by the sole application of mordants followed by dyeing in the tub. In the latter case, the colouring matter adheres only to the mordanted designs, the latter retaining the shade desired, and the ground of the stuff preserving its original colour after being washed.

Colouring matters printed directly on stuffs should be thickened, so that they will not run, and that the designs may retain their sharpness. The thickening substances used are starch, gum-senegal, and gum-tragacanth, to which a certain quantity of pipe-clay, and sometimes of gelatin, is often added. The stuffs should be previously mordanted, or the mordant incorporated with the colour.

§ 1748. In order to explain how designs are produced by dyeing, we shall give some examples. Let us suppose that a red design is to be produced on a white ground: the design is then printed on the stuff with a thickened mordant of alum, and the stuff passed through the madder-tub; when the colouring matter adheres firmly only to the mordanted design, which alone will remain red after washing. If, on the contrary, a white picture is to be produced on a red ground, the picture is first printed with a properly thickened oleaginous substance, and passed through the mordant, by which means the picture is *reserved*, and when the stuff is passed through the madder-tub the ground alone will be dyed red. Another method still may be employed by dyeing the stuff of a uniform red colour, and printing the design with a non-volatile vegetable acid, such as, for example, citric or tartaric, sufficiently thickened; after which it is passed through a bath of hypochlorite of lime, which immediately destroys the picture, without attacking the ground. This process is called *discharging the colour*.

In order to obtain a violet design on a more or less deep red ground, the stuff is mordanted with alum, and the design printed



with a thickened mordant of iron, and then passed through the madder-tub; when the ground will become red, and the design violet. If, on the contrary, a red design on a violet ground is desired, the stuff is passed through a mordant of alumina, and the design printed with an oily substance; and after being mordanted with acetate of iron, the oily reserve is removed by alkaline lyes, and the stuff is passed through the madder-tub.

Designs of more than two colours are obtained by machines composed of several cylinders, each of which prints a peculiar mordant, or reserve, or acid on the stuff, which then passes into the different dye-vats. Although the processes described are far from being the only ones used in dyeing, they will serve to give a general idea of the art.

#### *Fixing of Colours by Steam.*

§ 1749. Many colours are more firmly fastened and afford more beautiful shades when the dyestuffs are exposed to the action of steam. Under the influence of heat, the woven fabric and colouring matters become more closely combined, and the shades are often modified in a peculiar manner.

#### TANNING.

§ 1750. Skins of animals soon become putrid in moist air; and although they will preserve for a long time in dry air, they become hard and brittle. The intention of tanning is to combine the animal substance with a certain quantity of tannin, which renders them imputrescible, and gives them softness and impermeability; while the latter properties are still further increased by the process of *currying*. A tanned hide is called *leather*. Three kinds of skins are used in tanning: *green hides*, or the fresh skins brought to the tanner soon after the death of the animal; and *dry* and *salt hides*, which come from foreign countries, chiefly from South America. Hides are divided into two kinds: *soft hides*, which retain their suppleness after tanning, and *hard hides*, which, on the contrary, are to be very hard, and as impervious as possible. Soft hides are made from the skins of cows, calves, horses, etc.; while those of the ox and buffalo are reserved for hard hides. Very thin and soft hides are prepared from the skins of sheep and goats, which are used for making gloves or in the manufacture of morocco.

Skins intended for soft hides are subjected to a previous washing in running water, in order to soften and *soak* them, and remove all their soluble principles; which operation lasts only for 2 or 3 days for green skins, but for a much longer time for dry or salt skins, because the latter must be submitted to several washings, treadings, and stretchings, before they acquire the necessary pliancy.

After being soaked, the skins are carried to the *scalding-vats*,

consisting generally of five vessels filled with milk of lime, of greater or less strength. The skins pass successively through them, commencing with the weakest. Each vat contains from 200 to 300 skins; the whole operation lasting 3 or 4 weeks.

This being done, the hair is removed, by scraping the skins from above downward, with a dull knife; after which they are washed and worked on the horse-beam: 1st. In order to remove any scraps of flesh which might adhere to them; 2dly. To remove the useless portions, and the edges, which are always thicker than the other parts; 3dly. To smooth the asperities which cover the skin on the hairy side, which is done with a piece of well-cemented, hard sandstone; 4thly. To completely cleanse both sides of the skin, which is done with a circular knife, wetting the skin frequently. After these various operations, the skins are *raised*; that is, they are left for several days in weak acids, for which purpose the *ooze*, (*jusée*,) or infusion of *tan*, is generally used, consisting of the tan exhausted by the tanning of skins in the vats, and which, after having become acid in the air, contains a certain quantity of lactic acid. During the first four days, the skins are removed every day, fresh ooze being added each time; after which they are allowed to remain for 3 or 4 days in the ooze, and are then carried to a weak infusion of new tan, where they remain for 15 days, increasing the strength of the liquid from time to time. They thus undergo a kind of preliminary tanning, and are prepared for the ultimate tanning, in the vats. The latter, which are of mason-work, are first charged with a layer of old tan, about 0.15 m. in thickness, then with a layer of fresh tan, only a few centimetres thick; after which the skins are laid upon each other, being separated by layers of tan; and lastly, above the last coat of tan a layer of old tan is placed, 0.3 m. in thickness; when the whole is covered with boards, kept down by heavy stones. Enough water is then let in to moisten the whole mass, dissolve the tannin, and bring it successively in contact with the skins. The vats thus filled, and containing 600 or 700 skins, are left for 5 or 8 months, during which time the skins are only once taken out, in order to renew the tan between them.

§ 1751. In making coarse leather, the scalding, which here is not sufficiently efficient, is replaced by a slight putrid fermentation of the skins, in rooms warmed by steam. The hair is then removed in the ordinary way, and they are placed in the ooze, the raising being accelerated by the addition of a small quantity of sulphuric acid from time to time; after which they are buried with the tan in the vats, where they are left for 18 months or two years.

Hides may be tanned much more rapidly, by keeping the swollen skins for 2 or 3 weeks in infusions of tan, which are frequently replaced by stronger ones. The leather thus made is not so strong, and has a deep colour, which keeps down its price.

§ 1752. After being tanned, the hides are cleaned on tables, with

brushes, and then dried in the air, when they are hammered or rolled, so as to give them the proper consistence; after which they are sold to the currier, when they undergo various mechanical operations, and are impregnated with fatty substances, according to the uses to which they are destined. Leather is generally coloured black with acetate of iron, made by dissolving scraps of old iron in sour beer; several coats of this salt being passed over the surface of the leather; when the tannin combines with the protoxide of iron, which, by the action of the air, passes into the state of sesquioxide, and produces a very intense black.

§ 1753. The sheep and kid skins used for glove making are cleaned by smearing the fleshy side with a mixture of lime and orpiment, when in 24 hours the hair comes off with the greatest ease. The skins are then worked into various shapes on the beam, and are then immersed for 3 weeks in winter, and only 2 or 3 days in summer, in a bran-bath, which, by fermentation, produces lactic acid, and effects the raising of the skins. The latter are then made imputrescible, not by tannin, but by chloride of aluminum, for which purpose they are dipped into a hot solution, containing, for each skin, 600 to 900 gm. of alum, and 150 to 200 gm. of sea-salt. They are then bleached, by immersion for 12 hours in a bath composed, for each skin, of 600 or 700 gm. of flour, and the half of the yolk of an egg, which is beaten to the consistence of honey, adding the tepid liquor which was used for aluming. The skins are then dried, and subjected to various mechanical operations.

§ 1754. Morocco is chiefly made from goat-skins, which, after being fleshed, and deprived of their hair by lime, are washed for a long time with the greatest care, in order to entirely remove the lime, which would injure their quality; and to effect this more perfectly, they are left for 24 hours in a bath of sour bran. Skins intended to be dyed red are sewn together by twos, the fleshy side within, so as to form a bag which will hold air; after which they are dipped into a bath of chloride of tin, which acts as a mordant, and subsequently into one of cochineal, to dye them. After being rinsed, one side of the bag is ripped open, and the tanning matter introduced, the latter in this case consisting of sumac, which is much richer in tannin than tan is; and they are then stirred for 4 hours in a weak solution of sumac, where they are left for two days. Morocco which is to be dyed of any other colour than red is tanned before being dyed; and in all cases the skins are subjected to numerous mechanical operations before being fit for sale.

#### CARBONIZATION OF WOOD AND BITUMINOUS COAL.

§ 1755. The greater portion of charcoal used is made in the woods, by *carbonizing wood in pits*.\* On a very hard hearth, three or four

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\* The American technical term "pits," for the heaps of wood to be carbonized,

large sticks, forming a chimney of from 0.25 m. to 0.30 m. in length, are arranged vertically; and around this chimney the wood is set upright, in three different stories, the diameters of which diminish successively, so as to form the trunk of a cone resting on its larger base. The largest sticks are placed nearest the axis of the kiln, and the smallest, with the branches, near the surface; after which the pit-kiln is covered with earth, leaves, and coal-dust arising from preceding operations. Holes pierced through the base of the pit allow of the introduction of the air necessary to combustion.

When the pit is built, a fire of pine-wood is made in the chimney, and kept up for 2 or 3 hours, at the end of which time it has communicated to the neighbouring logs, and the chimney is almost wholly filled with small charcoal: it is then covered, and holes, which act as chimneys and draw combustion to the parts they penetrate, are made around the upper part of the pit. Thick, white smoke at first escapes, but it soon becomes transparent and bluish, which is a sign that combustion is progressing in the upper part of the kiln. The upper holes are then closed, and others made somewhat lower down, which are again closed when the same smoke again appears, others being made, and so on, until the bottom of the pit is reached. Carbonization thus extends from above downward; and the surface of separation of the carbonized wood and that yet untouched by the fire, is an inverted cone, having the same axis with that of the pit, and spreading more and more as carbonization advances, to be at last lost in the base of the pit. The wood diminishes considerably in volume by carbonization, and the pit becomes smaller. When carbonization is terminated, the openings are closed, and the fire is allowed to go out, after which the heap is overturned, and the imperfectly carbonized pieces are picked out, which would smoke in the fire.

The gases evolved during combustion are composed of nitrogen, which proceeded from the air used in combustion; carbonic acid and oxide, produced partly by active combustion of the wood, and partly by its calcination; hydrogen; vapour of water; and several organic substances furnished by the distillation of the wood, among which may be distinguished acetic acid, wood-spirit, and tarry substances. The relative proportion of all these products varies at the different stages of the process.

Wood yields, by carbonization in pits, about 15 per cent. of charcoal, and 25 to 30 by distillation in close vessels; but the latter process is one adopted with advantage only in the making of pyroligneous acid and tar, the charcoal thus obtained being not much valued on account of its lightness.

§ 1756. Bituminous coal is often carbonized in pits in the vicinity

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must not be confounded with the usual meaning of the word. The German name *meiler* is used in England.—*W. L. F.*

of the mines. The pits generally receive an elongated prismatic shape, and contain horizontal, longitudinal, and transverse canals, besides vertical chimneys, for the circulation of air. The largest lumps of coal are placed on the inside and the smallest on the outside; while the covering is made of coal-dust and coke, moistened to give it more consistence. The process closely resembles that of making wood-charcoal.

Coke is also made by subjecting the bituminous coal to imperfect combustion in furnaces, where the ingress of air is so regulated as to consume the least possible quantity of carbon.

Lastly, coke is obtained by the distillation of bituminous coal in retorts, the principal product being illuminating gas, while the coke is only an accessory product; and as it is very light, it is used only for domestic purposes.

#### ILLUMINATING GAS.

§ 1757. Illuminating gas is generally obtained from the calcination of bituminous coal; but all kinds are not equally adapted to the purpose, the best being those designated (§ 1315) under the name of *bituminous coal burning with a long flame*. The coals of Mons and Commentry, which are generally used in Paris, yield on an average 23 cubic metres of gas for 100 kilog. Distillation is effected in large cylindrical cast-iron retorts, ranged parallel to each other, to the number of 2, 3, or 5, over the same furnace; each retort being provided with a vertical tube, through which the coal is introduced, and to which is fastened the pipe for the discharge of the gas. The temperature of the furnace should be kept at a bright cherry red, because, if it is greater, the gas does not give much light, for the bicarburetted hydrogen gas, and the very volatile oils, to which the brilliancy of the flame is chiefly owing, deposit carbon, and are converted into protocarburetted hydrogen, the combustion of which gives but little light; and if, on the contrary, the temperature is too low, a large quantity of essential oil is formed, which cannot remain in suspension in the gas, but is deposited in the refrigerators. The duration of distillation varies according to the quality of the coal, its hygrometric state, and the arrangement of the apparatus; and the residue consists of a light coke, much used for domestic purposes.

The gas produced by the distillation of bituminous coal is composed chiefly of protocarburetted hydrogen, mixed with various quantities of bicarburetted hydrogen, hydrogen, oxide of carbon, carbonic acid, nitrogen, oleaginous matters more or less easily condensed, ammoniacal and sulphuretted compounds, and tarry substances. As in this state it exhales a very fetid smell, and the products of its combustion are themselves odoriferous, it is necessary to purify it, especially for domestic use; to which effect it is conveyed from the retort into a small barrel, partly filled with water, through a pipe entering the liquid to the depth of 2 or 3 centimetres, so as to intercept the communication of the retort with the

apparatus in which the gas is collected. The greater part of the water and tar condenses in the barrel, which is furnished with a discharging-pipe to maintain a constant level in the barrel, and to allow the excess of the condensed products to escape. The gas on leaving the barrel traverses a series of pipes more or less cooled, in which the condensation of the water and tar is completed, is then conducted through boxes containing metallic salts, chiefly chloride of manganese and sulphate of iron, which decompose the ammoniacal salts, and isolate the sulphydric acid; and finally passes through other boxes containing hydrated lime, which absorbs the sulphydric gas, the carbon acid, and the other acid vapours. But these purifications must not be pushed too far, because the gas would be deprived of too much of its oily vapours, and its illuminating power would be sensibly decreased.

The gas is collected in *gasometers*, resembling immense bells, made of sheet-iron, and inverted in cisterns of corresponding size, built of hydraulic mason-work, and filled with water. The weight of the gasometer is partially balanced by counterpoises, which should leave it only the weight necessary to the pressure required for the distribution of the gas to the various jets it is to feed. The pressure is composed of, 1st. The resistance which the gas meets in circulating through pipes ordinarily of great extent; 2dly. The excess of elastic force which it must retain in order to feed the jets; 3dly. The pressure necessary to drive it to the highest points, the level of which is often higher than that of the gasometer. The last pressure may be easily calculated after ascertaining the difference  $h$  of the level of the gasometer and the highest jet, and the density  $d$  of the gas as compared to that of the air, when it is equal to the weight of a column of water, the height of which is represented by  $0.001293\ h d$ .\*

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\* A more economical process of manufacturing gas has recently been put in operation in Manchester, England. Three or five retorts are used, the central one of which is charged with metallic iron and coke, or with coke alone, and traversed by a current of steam, which thus is decomposed into hydrogen and oxygen. These gases are led through the other retorts, in which coal is being distilled, when the free hydrogen combines with the nascent carbon resulting from the decomposition of different hydrocarbons, and forms olefiant gas, which imparts a great brilliancy to the flame. The gas thus manufactured is called *hydrocarbon* gas; and I had opportunity to assure myself that its illuminating power is double that of ordinary gas under the same circumstances, while the cost of producing it is at least not higher.—*W. L. F.*



## GENERAL INDEX.

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- |  |   |
|--|---|
| <p>             Acetates, ii. 546.<br/>             Acetic acid, ii. 542.<br/>             Acetone, ii. 549.<br/>             Acids, vegetable, ii. 594.<br/>             Aconitic acid, ii. 597.<br/>             Acumination of crystals, i. 18.<br/>             Adipic acid, ii. 697.<br/>             Air, analysis of, by the eudiometer, i. 129.<br/>             Air, atmospheric, i. 119.<br/>             Air, only a mixture, i. 131.<br/>             Air-thermometer, (note,) ii. 414.<br/>             Albumen, ii. 453.<br/>             Albuminous vegetable substances, ii. 451.<br/>             Alcarsin, ii. 551.<br/>             Alcohol, ii. 511.<br/>             Alcoholic fermentation, ii. 505.<br/>             Alcoholometry, ii. 513.<br/>             Alcohol and ether, oxidation of, ii. 541.<br/>             Aldehyde, ii. 541.<br/>             Alkalimetry, i. 448.<br/>             Alkaline earths, their separation and determination, i. 564.<br/>             Alkaline metals, i. 434.<br/>             Alkalino-earthly metals, i. 528.<br/>             Alkaloids, ii. 612.<br/>             Alloys, i. 377.<br/>             Allyl, ii. 675.<br/>             Almaden, extraction of mercury at, ii. 291.<br/>             Aluminum, i. 567.<br/>             Alumina, salts of, 570.<br/>             Alumina, characters of the salts of, i. 578.<br/>             Alumina, silicates of, i. 575.<br/>             " sulphates of, i. 570.<br/>             Alums, manufacture of, i. 571.<br/>             Amalgams, ii. 289.<br/>             Ammonia and alkalies, determination of, i. 572.<br/>             Ammonia, behaviour of potassium and sodium to, i. 520.<br/>             Ammonia, carbonates of, i. 520.         </p> | <p>             Ammonia, chlorohydrate of, i. 516.<br/>             " compounds of, i. 514.<br/>             " phosphates of, i. 519.<br/>             " sulfhydrate of, i. 518.<br/>             Ammoniacal salts, distinctive character of, i. 521.<br/>             Ammoniacal solution, action of the battery on an, i. 521.<br/>             Amygdalin, ii. 650.<br/>             Amylaceous substances, ii. 461.<br/>             Amylammonia, ii. 624.<br/>             Amylic alcohol, ii. 665.<br/>             Amylic ethers, ii. 669.<br/>             Analysis, i. 138.<br/>             " of gases, ii. 422.<br/>             " proximate, of organic substances, ii. 363.<br/>             " ultimate, of organic substances, ii. 366, 386.<br/>             Anilin, ii. 621.<br/>             Animal chemistry, ii. 719.<br/>             " heat, ii. 734.<br/>             Anisic acid, ii. 662.<br/>             Antimony, ii. 211.<br/>             " alloys of, ii. 221.<br/>             Antimony, analytic determination of, ii. 219.<br/>             Antimony, behaviour of salts of, ii. 213.<br/>             " chlorides of, ii. 217.<br/>             Antimony, detection of in poisoning, ii. 221.<br/>             Antimony, metallurgy of, ii. 222.<br/>             " oxides and acids of, ii. 212.<br/>             " salts of, ii. 214.<br/>             " sulphides of, ii. 215.<br/>             Arabin, ii. 468.<br/>             Arseniates and arsenites, determination of, i. 429.<br/>             Arsenic acid, i. 282.<br/>             " " antidotes to poisoning by, i. 285.<br/>             " " its preparation, i. 280.         </p> |
|--|---|



- Arsenic acid, its properties, i. 279.  
 Arsenic acid, researches in poisoning by, i. 285.  
 Arsenious acid, analysis of, i. 281.  
     " " properties of, i. 281.  
 Arsenious acid, detection of, in animal matter, i. 289.  
 Asparagin, ii. 627.  
 Atmosphere, action of plants on the, ii. 716.  
 Atmospheric air, i. 119.
- B.**
- Balsams, ii. 660.  
 Bar-iron, composition of, ii. 116.  
     " from cast-iron, ii. 82.  
 Bassorin, ii. 468.  
 Barium, and its oxides, i. 528.  
     " chloride of, i. 533.  
     " sulphide of, i. 533.  
 Baryta, salts of, i. 532.  
 Baryta, distinctive character of the salts of, i. 534.  
 Beet-sugar, manufacture of, ii. 771.  
 Belgium, reduction of zinc in, ii. 147.  
 Benzamide, ii. 643.  
 Benzil, ii. 648.  
 Benzin, ii. 648.  
 Benzoic acid, ii. 644.  
     " ethers, ii. 645.  
 Bezoaric acid, ii. 609.  
 Bile, ii. 746.  
 Biliary calculi, ii. 747.  
 Bismuth, ii. 204.  
     " alloys of, ii. 208.  
 Bismuth, analytic determination of, ii. 208.  
 Bismuth, metallurgy of, ii. 209.  
     " oxides of, ii. 205.  
     " salts of, ii. 206.  
 Bitter almonds, oil of, ii. 642.  
 Blast-furnace, ii. 66.  
 Bleaching by chlorine, i. 218.  
     " by sulphurous acid, i. 177.  
     " salt, manufacture of, i. 551.  
 Blistered steel, ii. 104.  
 Blood, analysis of, ii. 742.  
     " coagulum, ii. 740.  
     " circulation of the, ii. 732.  
     " globules, ii. 739.  
 Blooming iron, ii. 92.  
 Blowpipe, hydroxygen, i. 92.  
     " with atmospheric air, i. 87.  
 Blue vitriol, ii. 240.  
 Bodies, simple and compound, i. 10.  
     " states of, i. 11.  
 Bodies, external characters used to distinguish, i. 13.  
 Bohemian glass, i. 627.  
 Boiling points of saline solutions, i. 410.  
 Bone, ii. 721.  
 Bone-black, decoloring power of, i. 307.  
     " manufacture of, ii. 777.  
 Boracic acid, i. 292.  
     " analysis of, i. 295.  
 Boracic ether, ii. 532.  
 Borates, determination of, i. 430.  
 Borax, manufacture of, i. 491.  
     " test, i. 493.  
 Borneo camphor, ii. 640.  
 Boron, i. 292.  
     " action of the metals on, i. 377.  
     " equivalent of, i. 295.  
     " fluoride of, i. 296.  
 Brake-table, ii. 20.  
 Brass, ii. 264.  
     " analysis of, ii. 270.  
 Brass and copper turning, ii. 269.  
 Bread, making, ii. 764.  
 Brewing, ii. 766.  
 British gum, ii. 486.  
 Bromates, determination of, i. 426.  
 Bromic acid, i. 241.  
 Bromides, i. 423.  
     " properties of metallic, i. 387.  
 Bromine in organic bodies determined, ii. 386.  
 Bromine, preparation and properties of, i. 240.  
 Bromohydric acid, i. 242.  
 Brucin, ii. 617.  
 Butter, making, ii. 752.  
 Butyric acid, ii. 574.  
     " fermentation, ii. 569.  
 Butyramide, ii. 574.
- C.**
- Cacodyl, ii. 551.  
 Cadmium and its compounds, ii. 153.  
 Cafein, ii. 618.  
 Calcium, determination of the equivalent of, i. 538.  
 Calcium, distinctive character of the salts of, i. 557.  
 Calcium, oxides of, i. 537.  
 Calcium, sulphide, chloride, and fluoride of, i. 556.  
 Calculi, urinary, ii. 762.  
 Calico printing, ii. 787.  
 Calomel, ii. 282.  
 Camphilen, ii. 637.  
 Camphor, ii. 639.  
 Candles, stearic acid, ii. 690.  
 Cane-sugar, ii. 470.  
     " manufacture of, ii. 773.  
 Cannon casting, ii. 266.  
 Cantharidin, ii. 626.  
 Caoutchouc, ii. 671.  
 Capric acid, ii. 699.  
 Caproic acid, ii. 699.  
 Caprylic acid, ii. 699.

- Caramel, ii. 471.  
 Carbollic acid, ii. 682.  
 Carbonated waters, i. 311.  
 Carbonates, determination of, i. 430.  
 Carbon, action of on metals, i. 377.  
 Carbon, hydrogen, and oxygen, analysis of compounds of, i. 323.  
 Carbon, nitrogen, compounds of, i. 337.  
     " oxygen, compounds of, i. 309.  
     " sulphur, compounds of, i. 333.  
     " different forms of, i. 304.  
     " organic determination of, ii. 367.  
 Carbonic acid, analysis of gaseous, i. 316.  
     " liquid and solid, i. 313.  
 Carbonic acid, preparation and properties of, i. 309.  
 Carbonic ethers, ii. 533.  
 Carbonic oxide, eudiometric analysis of, i. 321.  
 Carbonic oxide, preparation of, i. 319.  
 Carburet of iron, ii. 53.  
 Carotin, ii. 709.  
 Cartilage, ii. 722.  
 Casein, ii. 748.  
     " vegetable, ii. 460.  
 Cassius's purple, ii. 325.  
 Cast-iron, ii. 53.  
     " analysis of, ii. 111.  
     " composition of, ii. 116.  
     " reduced to bar, ii. 82.  
 Castor-oil, ii. 700.  
 Cast-steel, ii. 104.  
 Catalonian forge, ii. 61.  
 Caustic, lunar, ii. 297.  
 Cedrin, ii. 641.  
 Cellulose, ii. 446.  
 Cementing apparatus, i. 622.  
 Cement, manufacture of hydraulic, i. 616.  
 Cerasin, ii. 468.  
 Cerebral substance, ii. 728.  
 Cerin, ii. 703.  
 Cerium, i. 583.  
 Charcoal, i. 592.  
 Charcoal, power of to condense gases, i. 307.  
 Charring wood, ii. 790.  
 Cheese, ii. 753.  
 Chemical affinity, i. 12.  
 Chemical and physical phenomena, difference between, i. 9.  
 Chemical nomenclature, i. 93.  
 Chemical notation and formulas, i. 73.  
 Chemistry, definition of, i. 10.  
 Chelidonic acid, ii. 611.  
 Chloral, ii. 561.  
 Chlorates, i. 425.  
 Chloric acid, i. 219.  
 Chlorides, determination of, i. 423.  
 Chlorides, metallic, preparation and properties of, i. 386.  
 Chlorometry, i. 552.  
 Chlorine and hydrogen, compounds of, i. 230.  
 Chlorine and nitrogen, compounds of, i. 227.  
 Chlorine and oxygen, compounds of, i. 219.  
 Chlorine, behaviour of to metallic oxides, i. 385.  
 Chlorine, bleaching by, i. 218.  
     " equivalent of, i. 228.  
     " preparation of, i. 215.  
     " organic determination, ii. 336.  
 Chloroform, ii. 586.  
 Chlorohydric acid and its compound, i. 230.  
 Chlorohydric ether, ii. 536.  
 Chlorophyll, ii. 709.  
 Chlorous acid, i. 225.  
 Chloroxycarbonic gas, i. 321.  
 Cholesterin, ii. 647.  
 Cholic acid, ii. 746.  
 Chromates, ii. 125.  
 Chronic acid, ii. 122.  
 Chromium, analytic determination of, ii. 128.  
 Chromium, oxides of, ii. 118.  
     " salts of, ii. 123.  
 Chyle, ii. 748.  
 Cider, ii. 768.  
 Cinnabar, ii. 281.  
 Cinnamic acid, ii. 659.  
 Cinnamon, oil of, ii. 658.  
 Cinchonin, ii. 614.  
 Citric acid, ii. 596.  
 Circular polarization, (note,) ii. 454.  
 Clay, i. 652.  
 Cleavage of crystals, i. 15.  
 Cloves, oil of, ii. 665.  
 Coal, table of composition of, ii. 500.  
     " varieties of, ii. 496.  
 Cobalt, analytic determination of, ii. 133.  
     " oxides of, ii. 130.  
     " salts of, ii. 131.  
 Cochineal, ii. 710.  
 Codein, ii. 617.  
 Cohesion, i. 12.  
 Coin, ii. 312.  
 Coking coal, ii. 790.  
 Collodion, ii. 492.  
 Colouring matters, organic, ii. 704.  
 Columbium, ii. 174.  
 Concrete, manufacture of, i. 618.  
 Conicin, ii. 620.  
 Coumarin, ii. 661.  
 Copper, ii. 236.  
     " alloys of, and zinc, ii. 263.  
     " " tin, ii. 265.  
     " analytic determination of, ii. 245.  
     " and brass, tinning, ii. 269.  
     " chlorides of, ii. 244.  
 Copper, English process of smelting, ii. 256.

- Copper, Mansfeld process of smelting, ii. 249.  
 Copper, metallurgy of, ii. 247.  
   " oxides of, ii. 237.  
   " salts of, ii. 239.  
   " sulphides, ii. 243.  
 Creatin, ii. 724.  
 Creasote, ii. 683.  
 Crucibles, i. 667.  
 Crystalline forms, six systems of, i. 20.  
   1. Regular system, i. 21.  
   2. Dimetric, i. 25.  
   3. Hexagonal, i. 30.  
   4. Trimetric, i. 36.  
   5. Monoclinic, i. 40.  
   6. Triclinic, i. 42.  
 Crystallization of the metals, i. 367.  
   " water of, i. 398.  
 Crystallography, i. 14.  
 Crystals, axes of, i. 19.  
   " cleavage of, i. 15.  
   " fundamental forms of, i. 15.  
   " imperfections of, i. 55.  
 Cumin, cuminic acid, ii. 664.  
 Cupellation, ii. 198, 313.  
 Cyanides, i. 424.  
 Cyanhydric or prussic acid, i. 342.  
 Cyanhydric or prussic acid, analysis of, i. 344.  
 Cyanogen, analysis of, i. 339.  
 Cyanogen, origin and preparation of, i. 338.  
 Cyanogen, products of, ii. 630.
- D.
- Decoloring power of bone black, i. 307.  
 Deliquescence and efflorescence, i. 98.  
 Density of vapours, ii. 406.  
 Deposit-trough for ores, ii. 18.  
 Deutoxide of nitrogen, i. 145.  
 Dextrin, ii. 485.  
 Diastase, ii. 487.  
 Didymium, i. 583.  
 Digestion, ii. 730.  
 Dimorphism and polymorphism, i. 60.  
 Distillation of oil of vitriol, i. 179.  
   " phosphorus, i. 256.  
 Dry distillation of organic bodies, ii. 678.  
 Ductility of metals, i. 368.  
 Dutch liquid, ii. 523.  
 Dyeing, principles of, ii. 781.
- E.
- Earthenware, various kinds, i. 664, 667.  
   " glaze for, i. 666.  
   " analysis of, i. 671.  
 Earths, analytic determination of, i. 594.  
 Earthy metals, i. 569.  
 Ellagic acid, ii. 609.
- Elements, classification of, i. 76.  
   " tabular view of, i. 64.  
 Emulsin, ii. 651.  
 Enanthic acid, ii. 670.  
 Engraving by fluohydric acid, i. 251.  
 Equisetic acid, ii. 596.  
 Erbium, i. 583.  
 Essential oils, ii. 634.  
 Ethal, ii. 701.  
 Ether, ii. 516.  
 Ethers, compound, ii. 529.  
 Ethionic acid, ii. 522.  
 Ethyl theory, (note,) ii. 568.  
 Ethylammonia, ii. 622.  
 Eudiometer, i. 104.  
 Eudiometer, analysis by the, i. 129, 145, 321.  
 Eugenic acid, ii. 665.  
 Euxanthic acid, ii. 708.  
 Evaporation, i. 100.  
   " of salines, i. 500.  
 Excrements, ii. 763.  
 Excretions, ii. 754.
- F.
- Fats, ii. 684.  
 Ferment, ii. 507.  
 Fermentation, alcoholic, ii. 505.  
   " butyric and lactic, ii. 569.  
 Fibrin, ii. 724.  
   " vegetable, ii. 460.  
 Fire-brick, i. 667.  
 Flame, the nature of, 487.  
 Flameless lamp, ii. 341.  
 Fluohydric acid, analysis of, i. 251.  
   " " engraving by, i. 251.  
   " " preparation of, i. 250.  
 Fluorides, analytic determination of, i. 424.  
 Fluorine, i. 424.  
 Fluor-spar, i. 556.  
 Fluosilicic acid, i. 301.  
 Forge-hearth, ii. 83.  
 Forge-steel, ii. 103.  
 Formic acid, ii. 583.  
 Formula, construction of organic, ii. 387.  
 Freiberg, extraction of silver at, ii. 305.  
 Frigorific mixtures, i. 412.  
 Fruit-sugar, ii. 474.  
 Fuel, mineral, ii. 494.  
 Fulminating mercury, ii. 279.  
   " silver, ii. 295.  
 Fulminic acid, ii. 632.  
 Fumaric acid, ii. 596.  
 Fuming sulphuric acid, i. 185.  
 Fusible metal, ii. 208.
- G.
- Gallic acid, ii. 607.  
 Galvanic gilding and silvering, ii. 333.

Galvanoplastics, ii. 335.  
 Garlic, oil of, ii. 675.  
 Gases, analysis of, ii. 422.  
     " collection of, over mercury, i. 94.  
 Gases, condensation of, by charcoal, i. 307.  
 Gases, solubility of, in water, i. 101.  
 Gasometer, i. 82.  
 Gastric juice, ii. 744.  
 Gelatin, ii. 726.  
 Gelatinous principles in plants, ii. 478.  
 Geology, i. 351.  
 Geological division of the formations, i. 361.  
 German silver, ii. 138.  
 Gilding, ii. 331.  
     " galvanic, ii. 338.  
 Glass, analysis of, i. 648.  
     " blowing on the table, i. 642.  
     " composition of, i. 623.  
     " kinds of, i. 626.  
     " manufacture of, i. 627-640.  
     " properties of, i. 641.  
 Glaze, i. 659.  
 Glucic acid, ii. 476.  
 Glucinum and its compounds, i. 579.  
 Glucose, manufacture of, ii. 487.  
 Glue, ii. 726.  
 Gluten, ii. 460.  
 Glycerin, ii. 689.  
 Glycocoll, ii. 727.  
 Glycyrrhizin, ii. 628.  
 Gold and its compounds, ii. 322.  
     " analytic determination of, ii. 326.  
     " alloys of, ii. 329.  
     " assay of, ii. 366.  
     " parting by acids, ii. 331.  
 Goniometer, i. 51.  
 Graduating glasses, i. 103.  
 Grape-sugar, ii. 475.  
 Gums, ii. 468.  
 Gun-cotton, ii. 491.  
 Gunpowder, analysis of, i. 608.  
     " composition of, 589.  
     " manufacture of, i. 595.  
 Gunpowder, testing the strength of, i. 606.  
 Gunpowder, theory of its effects, i. 587.  
 Gutta-percha, i. 673.

## H.

Hair, ii. 723.  
 Haloid salts, i. 397.  
 Hematosin, ii. 740.  
 Hemitrope crystals, i. 59.  
 Hexagonal system of crystals, i. 30.  
 Hippuric acid, ii. 760.  
 Horn, ii. 722.  
 Hot-blast, ii. 77.  
 Humin, ii. 489.

Hydraulic lime, i. 614.  
 Hydrogen, behaviour of to oxides, i. 383.  
     " equivalent of, i. 11.  
 Hydrogen, organic determination of, ii. 367.  
 Hydrogen, preparation of, i. 89.  
     " and arsenic, i. 282.  
     " and chlorine, i. 230.  
     " and iodine, i. 247.  
     " and nitrogen, i. 162.  
     " and oxygen, i. 96.  
     " and phosphorus, i. 270.  
     " and sulphur, i. 201.  
 Hydroxygen blowpipe, i. 92.  
 Hypochlorates, analysis of, i. 425.  
 Hypochloric acid, i. 227.  
 Hypochlorites, i. 467.  
 Hypochlorite of lime, i. 550.  
 Hypochlorous acid, i. 223.  
 Hyponitric acid, i. 155.  
 Hypophosphites, i. 428.  
 Hypophosphorous acid, i. 266.  
 Hyposulphates, i. 427.  
 Hyposulphite of soda, i. 494.  
 Hyposulphites, i. 428.  
 Hyposulphuric acid, i. 197.  
     " " sulphuretted, i. 197.  
 Hyposulphurous acid, i. 196.

## I.

Ichthyocolla, ii. 727.  
 Idria, extraction of mercury in, ii. 290.  
 Illuminating gas, ii. 792.  
 Ilnenium, ii. 174.  
 Indigo, ii. 714.  
 Inosic acid, ii. 725.  
 Intestinal gases, ii. 763.  
     " juice, ii. 747.  
 Introduction to general chemistry, i. 9.  
 Introduction to organic chemistry, ii. 361-445.  
 Inulin, ii. 467.  
 Iodates, i. 426.  
 Iodides, metallic, i. 387.  
 Iodides, analytic determination of, i. 424.  
 Iodine, action of on the metals, i. 377.  
     " organic determination of, ii. 386.  
 Iodine, properties and preparation of, i. 244.  
 Iridium, ii. 353.  
 Iron, analytic determination of, ii. 54.  
     " analysis of cast, and steel, ii. 111.  
     " and its oxides, ii. 36.  
     " cast, converted into bar-iron, ii. 82.  
 Iron, composition of bar, cast, and steel, ii. 116.  
 Iron, dry assay of ores of, ii. 108.  
     " making steel, ii. 102.  
     " ores of, ii. 59.

Iron, reduction of the ores of, ii. 61.  
 " salts of, ii. 44.  
 " sheet, and tin-plate, ii. 98.  
 " wire-drawing, ii. 101.  
 Isatin, ii. 715.  
 Isomorphism, i. 61.

## J.

Japan camphor, ii. 639.  
 Jigging machine, ii. 16.

## K.

Kermes mineral, ii. 218.  
 Kyanole, ii. 621.

## L.

Lactic acid, ii. 573.  
 " fermentation, ii. 569.  
 Lactometry, ii. 750.  
 Lanthanum, i. 583.  
 Law of multiple proportions, i. 12.  
 Laws of combination of gases, i. 158.  
 " constitution of salts, i. 391.  
 Lead, alloys of, ii. 189.  
 " analytic determination of, ii. 188.  
 " and its oxides, ii. 174.  
 " casting shot, ii. 203.  
 " cupellation of, ii. 198.  
 Lead, desilverized by crystallization, ii. 202.  
 Lead, metallurgy of, ii. 190.  
 " red, or minium, ii. 178.  
 " salts of, ii. 179.  
 " " acetates, ii. 183.  
 " " carbonates, ii. 184.  
 " " behaviour of, ii. 186.  
 " sheet, and pipe, ii. 202.  
 " glass, i. 673.  
 Lemons, oil of, ii. 638.  
 Leucole, ii. 620.  
 Lichenin, ii. 467.  
 Lichens, ii. 710.  
 Lignin, ii. 449.  
 Lime, i. 537.  
 " for mortar, i. 611.  
 " hydraulic, i. 614.  
 " hypochlorite of, i. 550.  
 " kiln, i. 539.  
 " native carbonates of, i. 547.  
 " phosphates of, i. 549.  
 " salts of, i. 542.  
 Limestones, composition of, i. 615.  
 " analysis of, i. 618.  
 Litharge, ii. 175.  
 Lixiviation of nitre-beds, i. 456.  
 Logwood, ii. 706.  
 Lunar caustic, ii. 297.  
 Lustre, metallic, i. 365.  
 Lymph, ii. 743.

## M.

Madder, ii. 705.  
 Magnesia, i. 558.  
 " salts of, i. 559.  
 " phosphates of, i. 561.  
 " behaviour of salts of, i. 563.  
 Magnesium, i. 558.  
 Malic acid, ii. 595.  
 Manganese, and its oxides, ii. 23.  
 Manganese, analytic determination of, ii. 31.  
 Manganese, acids of, ii. 25.  
 " salts of, ii. 28.  
 Mannite, ii. 484.  
 Mansfeld, extraction of silver in, ii. 309.  
 " " copper in, ii. 249.  
 Margaric acid, ii. 692.  
 Marsh gas, i. 330, and ii. 582.  
 Marsh's apparatus for arsenic, i. 286.  
 Matches, phosphoric, i. 259.  
 Meconic acid, ii. 609.  
 Menthen, ii. 641.  
 Mercaptan, ii. 589.  
 Mercurial cistern, i. 94.  
 Mercury, ii. 271.  
 " amalgams, ii. 289.  
 Mercury, analytic determination of, ii. 288.  
 Mercury, chlorides of, ii. 282.  
 " metallurgy of, in Idria, ii. 290.  
 Mercury, metallurgy of, at Almaden, ii. 291.  
 Mercury, oxides of, ii. 273.  
 " salts of, ii. 275.  
 " sulphides of, ii. 281.  
 Mesitylen, ii. 550.  
 Metallic veins, i. 363.  
 Metals, i. 349.  
 " action of oxygen on, i. 374.  
 Metals, action of sulphur and chlorine on, i. 376.  
 Metals, action of other metalloids on, i. 377.  
 Metals, alkaline, i. 434.  
 " alkalino-earthly, i. 528.  
 " chemical properties of, i. 371.  
 " classification of, i. 372.  
 " crystallization of, i. 367.  
 Metals, malleability and ductility of, i. 368.  
 Metals, opacity, lustre, and colour of, i. 368.  
 Metals, physical properties of, i. 365.  
 " properties of oxides of, i. 380.  
 " " chlorides of, i. 386.  
 " relations of, to heat, i. 371.  
 Metalloids, i. 79.  
 " equivalents of the, i. 346.  
 Methylal, ii. 585.

Methylic alcohol, ii. 575.  
 " compounds, table of, ii. 591.  
 Methylic ethers, ii. 548.  
 Methylammonia, ii. 623.  
 Milk, ii. 748.  
 " sugar of, ii. 751.  
 Minium, ii. 178.  
 Mineral fuel, ii. 494.  
 " green, ii. 242.  
 Mirrors, ii. 289.  
 Molecular decrements, i. 44.  
 Molybdenum, ii. 233.  
 Monobasic and polybasic salts, i. 395.  
 Monoclinic system, i. 40.  
 Monometric " i. 21.  
 Mordant, ii. 785.  
 Morphin, ii. 615.  
 Mortar, i. 611.  
 Mucic acid, ii. 493.  
 " ether, ii. 536.  
 Multiple proportions, law of, i. 12.  
 Muscular tissue, ii. 723.  
 Mustard, oil of, ii. 676.  
 Myricin, ii. 703.  
 Myronic acid, ii. 677.

## N.

Naphtha, ii. 683.  
 Naphthalin, ii. 678.  
 Narcotin, ii. 616.  
 Nickel, analytic determination of, ii. 139.  
 Nickel, in German silver, ii. 138.  
 " oxides of, ii. 136.  
 " salts of, ii. 137.  
 Nicking-buddle, ii. 19.  
 Nicotin, ii. 618.  
 Niobium, ii. 174.  
 Nitrates and nitrites, determination of, i. 424.  
 Nitre-beds, i. 454.  
 Nitric acid, i. 133.  
 " analysis of, i. 138.  
 Nitric acid, formation and preparation of, i. 135.  
 Nitric acid, manufacture of, i. 137.  
 " ether, ii. 530.  
 " oxide, analysis of, i. 150.  
 Nitrils, ii. 629.  
 Nitrogen, i. 117.  
 Nitrogen and carbon, compounds of, i. 337.  
 Nitrogen and chlorine, compounds of, i. 227.  
 Nitrogen and hydrogen, compounds of, i. 162.  
 Nitrogen and iodine, compounds of, i. 248.  
 Nitrogen and oxygen, compounds of, i. 132.  
 Nitrogen and phosphorus, compounds of, i. 275.  
 Nitrogen, chemical and physical properties of, i. 119.  
 Nitrogen, deutoxide of, or nitric oxide, i. 145.  
 Nitrogen, equivalent of, i. 159.  
 Nitrogen, organic determination of, i. 380.  
 Nitrogen, preparation of, i. 119.  
 " protoxide of, i. 142.  
 Nitrous acid, analysis of, i. 154.  
 Nitrous acid, preparation and properties of, i. 153.  
 Nitrous matters, lixiviation of, i. 456.  
 Nutrition, ii. 729.

## O.

Oil of aniseed, ii. 662.  
 " bitter-almonds, ii. 642.  
 " cinnamon, ii. 658.  
 " garlic, ii. 675.  
 " mustard, ii. 676.  
 " spiræa, ii. 654.  
 " wine, ii. 528.  
 Oils, essential, ii. 634.  
 Olefant gas, ii. 520.  
 Oleic acid, ii. 693.  
 Opacity of the metals, i. 365.  
 Optical glass, ii. 639.  
 Ores, crushing, ii. 11.  
 " preparation of, ii. 9.  
 " stamping, ii. 17.  
 " washing, ii. 10.  
 Ornaments and painting of earthenware, i. 667.  
 Osmium, ii. 350.  
 " extraction of, ii. 352.  
 Oxalates of potassa, i. 467.  
 Oxalic acid, i. 322, ii. 594.  
 " ethers, ii. 534.  
 Oxides, preparation of, i. 381.  
 " determination of, i. 422.  
 Oxygen and arsenic, compounds of, i. 280.  
 Oxygen and carbon, compounds of, i. 309.  
 Oxygen and chlorine, compounds of, i. 219.  
 Oxygen and hydrogen, compounds of, i. 96.  
 Oxygen and nitrogen, compounds of, i. 132.  
 Oxygen and phosphorus, compounds of, i. 266.  
 Oxygen, preparation of, i. 79.  
 " properties of, i. 85.  
 Oxysaccharic acid, ii. 491.

